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WOOD WASTE REUSE IN CONTROLLED RELEASE PESTICIDES

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The utilization of large quantities of solid waste materials by chemical combination with pesticides is discussed. The associated expenditures and the disadvantages of the current methods of application for these pesticides are contrasted with the general advantages of the corresponding controlled release forms based on solid waste macromolecules. The preparation of such combinations is described. Theories which permit the prediction of the period of effectiveness of solid waste-pesticide combinations have been developed and validated. Solid waste - herbicide combinations based on 2,4-dichlorophenoxybutyric acid have been found to be capable of safely suppressing weeds and brush in the presence of conifers and field tests have shown that conifer growth is thereby substantially accelerated. The practicability of longacting controlled release forms of insecticides was also demonstrated.

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to solve the problem of solid waste management, this study, published by the National Environmental Research Center - Cincinnati, examines the use of solid wastes as a base for the preparation of controlled release pesticides. Environmental pollution both by solid wastes and pesticides could be reduced by combining the two and using them for a controlled release pesticide.

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ABSTRACT

The utilization of large quantities of solid waste materials by chemical combination with pesticides is discussed. The associated expenditures and the disadvantages of the current methods of application for these pesticides are contrasted with the general advantages of the corresponding controlled release forms based on solid waste macromolecules. The preparation of such combinations is described. Theories which permit the prediction of the period of effectiveness of solid waste-pesticide combinations have been developed and validated.

Solid waste herbicide combinations based on 2,4-dichlorophenoxybutyric acid have been found to be capable of safely suppressing weeds and brush in the presence of conifers and field tests have shown that conifer growth is thereby substantially accelerated. The practicability of long-acting controlled release forms of insecticides was also demonstrated by controlling the cedar and mahogany shootborer for one year in field trials under severe tropical testing conditions.

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INTRODUCTION

A prodigious amount of solid waste which is lignocellulosic or proteinaceous in nature is generated annually all across the nation. This totals about 165 million tons and can comprise such materials as bark, sawdust, and lignin from both the east and west coasts of the country, oat hulls, corn cobs, bran, bagasse and other agricultural residues from the midwest and the south as well as leather and cannery wastes from the southwest, and even king crab shells in Alaska.

The methods of disposing of this solid waste are as diverse as its sources but much of it is burned, which contributes to air pollution, while that which finds its way into our rivers and lakes makes its contribution to the pollution of our waterways. The magnitude of this disposal challenge[1] is emphasized by a recent Public Health Service Survey[2] which indicated that the per capita solid wastes generated each day are nearing 6 lb. Expressed in another way, nearly one in each ten dollars of every American community's budget is spent to collect and dispose of its solid wastes. The best estimate available indicates that in the U.S. a total of $3 billion is expended annually to remove and dispose of some 146 million tons of refuse.[3]

In considering useful ways of utilizing this variety of solid waste, it is important to emphasize the volumes available and their widespread national distribution. It thus is apparent that any application sought should preferably consume large volumes of the solid waste and should be useful in all parts of the country.

Although these solid wastes may seem extremely diverse in character, they do have a great deal in common. They are all polymeric in structure and can be so classified. For example, bark and sawdust solid wastes have much in common with the agricultural residual comprising oat hulls, corn cobs, bran, bagasse, etc; all are lignocellulosic. That is, all consist predominately of polymeric cellulose macromolecules. On the other hand, the leather and cannery wastes are classifiable together as polypeptides. Furthermore, both these classes have an important quality in common in that all members contain an abundance of replaceable hydrogen atoms and are biodegradable. Many of them, moreover, have fibrous structures which can be advantageous for many purposes. These materials then should be regarded as national assets rather than as liabilities. Taking into account these attributes of the solid wastes, the question of their disposal can then be rephrased as "How can a large quantity of low cost, biodegradable, reactive polymers, which are available nationwide, be best utilized?"

One answer to this question which the University of Washington is now investigating, broadly suggests that these polymeric solid wastes can be utilized by chemical combination with the pesticides in current widespread use. These pesticides, as presently known, have an intrinsic consumer value of almost $1 billion and have annual application costs of approximately $5 billion/year.[4] They are used to combat another national problem, the magnitude of which is not always appreciated. Their necessity is illustrated by the statistics which show that pests cause an estimated $15 billion annual loss in the value of forest, livestock, and agricultural production. Every year, various infestations destroy about 25% of crops, kill some 7 billion cu. ft. of timber, and prevent the production of 21 billion more by the slowing of growth. On a worldwide scale, fungi, weeds, and insects

destroy an estimated 20% of all foodstuffs before harvesting; during transportation and storage, an additional 10% is destroyed by various pests, including rodents. In addition, pests threaten health and mar enjoyment of recreational areas.

To minimize these depredations, government, industry, and private individuals in the U.S. spend approximately $5 billion annually. About 80% of this, including agricultural pest controls such as cultivation, is directed toward increasing agricultural efficiency. Some 50% ($2.5 billion) is spent to eliminate weeds in crops, pastures, rangelands, water systems, and right-of-ways; nearly 20% ($1 billion) is for control of insects. A detailed breakdown of this expenditure is given in Table 1.

However, in spite of the desirability of ameliorating these pest problems and the intrinsic effectiveness of the pesticides available the sophistication of the methods of application leave much to be desired. As a consequence, the efficiency of the pesticide in terms of the ratio of pesticide necessary to pesticide applied is low. Furthermore, the pesticides usually have rather short useful lives because they may be degraded by bacteria to inactive metabolites or washed by the rain into the subsoil where they are inaccessible to the pests they are intended to control.

This leaching into the subsoil often means that some rather stable pesticides presently used or their degradation products find their way into potable water supplies.[5-8] As a consequence, material of pesticide origin may end up in the human body and the long term health effects of this ingestion are far from clear. Suggestions that such accumulation of pesticide derivatives are a definite human health hazard have been

TABLE 1

ESTIMATED ANNUAL PEST CONTROL EXPENDITURES IN THE U.S.A.[1]

80% Agricultural ($4 billion)	20% Non-agricultural ($1 billion)
77% cultural practices, physical and mechanical control[2]	38% residential[5]
13% chemicals	34% pest control operators
5% pesticide application services[3]	10% industrial[6]
3% other research	10% highway right-of-ways
1% application equipment	3% railroad right-of-ways
1% surveillance, quarantine, methods of improvement[4]	3% insect wire screening
	2% public health[7]

1. According to USDA data totals $5 billion.
2. Includes expenditures for labour and for mechanical equipment such as cultivators, weeders, ploughs, harrows and stalk cutters.
3. Approximately 60% grower application cost, 40% custom applicators' service.
4. Biological control is chiefly performed as part of government and university research efforts.
5. Retail value of consumer pesticidal products.
6. Cost of industrial biocides (fungicides and preservatives).
7. Mostly mosquito vector abatement programme of state and local agencies.

repeatedly made, and it is, of course, well established [9] that conventionally applied pesticides can often be found in comestibles including fruit,[10] fish,[11] poultry,[12] meat,[13,14] vegetables,[15,16] eggs,[12] butter,[17] and milk[14,18] in appreciable quantities. While definite proofs have not yet been provided as to the precise dangers involved in the continued and prolonged consumption of these chemicals by humans, a prudent course would be to reduce and avoid such pesticide intake as far as practicable. Thus, for example, many of the more commonly used herbicides regarded as relatively innocuous by the public and used on their lawns, including 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) induce symptoms of acute and chronic toxicity in dogs[19] and other experimental animals[20] and affect the thyroid function in the rat.[21]

If in contrast, the pesticide were not generously broadcast but was to be chemically combined with the polymeric solid waste by displacement of a replaceable hydrogen atom, then its useful life should be prolonged since attack by bacteria should be reduced and the pesticide should not be leachable into the subsoil and hence to streams and rivers. As the solid waste-pesticide combination lies on and in the soil, it would gradually decompose, continuously releasing the active pesticide over a long period of time.[22,23]

As far as the authors are aware, their idea of disposing of solid waste in a useful fashion by chemical combination with pesticides to obtain a controlled action material is completely novel. Of course, the idea of sustained action pesticides is of itself not new and attempts to absorb pesticides on inert carriers or to enclose them in gelatin capsules or plastic forms have been disclosed in the literature.[22-81] Some of the

general advantages of controlled release solid waste combinations are as follows.

Disposal and Utilization of Solid Waste. It is obviously difficult to estimate how much solid waste would be reused but if we consider only urban solid waste problems alone without taking into account residues from agriculture, forestry, and food processing, it can be demonstrated that significant amounts of waste material could be involved. Thus, the total amount of paper and paperboard "going to the dump" every year amounts to about 40 million tons.[82] Recovery methods such as the "fiber claim system" being test-demonstrated at Franklin, Ohio, under an EPA grant may isolate 50% of the incoming waste paper; i.e., about 20 million tons a year on a national basis. However, substantial amounts (25%) of this lignocellulose waste, e.g., that contaminated with plastic, will not be suitable for recycling as paper.[83] This otherwise unusable material could be employed in controlled release pesticide combinations in amounts comparable to its output from recovery systems.

For example, the total area of forest lands in the U.S. is 5×10^8 acres.[84] On a 50-year cutting and planting cycle, 10^7 acres could be treated per year at a solid waste herbicide application level of 200 lb/acre. This in total would consume 1 million tons of recovered urban waste paper each year. By similar calculations, it can be shown that grazing land (3×10^8 acres)[84,85] agriculture (8.5×10^7 acres)[84,85] and highways (3.7×10^6 miles)[86,87] could each be expected to provide an outlet for considerable amounts of solid wastes. Thus, a total of roughly about 5 million tons of biodegradable waste could be recycled in controlled release pesticide combinations each year. This is equivalent to about 12% of the total cellulosic content in urban waste, 24% of the recoverable

cellulosic material and perhaps close to 100% of the plastic-contaminated paper in urban solid waste.[88] Less conservative use-penetration figures could, of course, increase these percentages substantially.

Easy-to-Handle Solid Material for Pesticidal Use. This is a well recognized advantage in pesticide usage and many pesticides are absorbed (but not chemically combined) on clays, crushed walnut shells or corn cobs to dilute and facilitate distribution of highly active materials over a large area. Thus, pesticide solid waste combinations could be easily handled, ground, chipped, etc., and distributed by conventional processes and machinery. New application techniques should therefore not need to be developed and air spraying, for example, should be more efficient and economical as no water would need to be carried as a diluent. The solid wood wastes are particularly suited for use in this way because they are rather uniform and aesthetically acceptable to the general public as soil amendments and garden mulches and, of course, they return organic matter to the soil. It is not expected that the performance of the solid waste-pesticide combination will be substantially affected by being on or in the soil surface. Furthermore, in this regard, it is worth noting that any pathogens in solid wastes, e.g., from proteinaceous sources such as manures, would be destroyed by the processing which attaches the pesticide.

Low Toxicity to Human and Wildlife. Many of the newer pesticides which are readily biodegradable and therefore desirable are highly toxic (see Table II). The organophosphates are especially noteworthy in this regard and efficient respiratory protective devices are recommended for persons handling these insecticides, even if absorbed on diluents.[89] Of course, when these materials are chemically combined rather than physically absorbed by the substrate they would become chemically nontoxic.

TABLE II

ORAL AND DERMAL TOXICITY OF SOME INSECTICIDES

Compound	Chemical Class	LD50 (mg/kg)	
		Oral	Dermal
Temik	Carbamate	0.79	3
Mevinphos (Phosdrin)	Organic Phosphorus	6	5
Phorate (Thimet)	Organic Phosphorus	2	6
Demeton (Systox)	Organic Phosphorus	1	14
Di-Syston	Organic Phosphorus	1	15
Parathion	Organic Phosphorus	1	21
Bidrin	Organic Phosphorus	2	43

Controlled Localized Continuous Release of Active Pesticide. By having a granular or tableted solid waste-pesticide combination, the active material can be more easily deposited in the precise location where it will do the most good. Aerial spraying of liquids and wind-drift can be thus avoided. This precise deposition and more effective one-shot application usage should lead to lower costs.

Lower Risk of Over-Application of Pesticide or Accidental Distribution by Spillage. By combining the pesticide with a solid waste, the problems and potential errors of measuring and diluting liquid concentrates are eliminated. Spillages of solids are, of course, less likely than liquid leakages and are easier to rectify when they occur.

Minimized Pollution Possibilities Caused by Migration of Pesticides to Waterways and Groundwater. Because the actual amount of pesticide needed for a biological response is so small, it can be anticipated that as this material is released under controlled conditions it will either be substantially absorbed by the host or trapped and degraded in the soil. By eliminating the distribution of mammoth amounts of pesticides, all at one time, saturation of the ecological environment will be avoided and the sudden rain washing of pesticides into waterways and ground water should be alleviated. This may permit the safe use of herbicides near irrigation canals and in areas where their use is currently dangerous and prohibited because of the proximity to crops especially sensitive to 2,4-D.

Introduction of New Biodegradable Pesticides. A specific advantage of solid waste-pesticide combinations which should be stressed is the potential of developing new extremely short-lived biodegradable pesticides which in combination with solid waste polymeric substrates would be sufficiently stable for practical use. For example, many organophosphorus pesticides,

such as octamethylpyrophosphoramide, are liquid and are too dermally toxic to permit their use by other than experts. Combination of these materials with solid waste substances would render them dermally safe whilst not destroying their biological activity. These currently "unusable" pesticides are also often effective at much lower dosages than the superficially less hazardous alternates currently permitted and used in relatively massive amounts. Also, since the pesticide solid waste combination would be "on-the-job" for a much longer period of the time than the current intermittent large pesticide applications, it can be assumed that the actual dosages present in the soil would be reduced by several orders of magnitude. For example, newly germinated weed seeds are often susceptible to incredibly minute quantities[90,91] of herbicides, but mammoth amounts are now conventionally applied to provide a duration of effectiveness by a "shear bulk" technique. Thus, this approach integrates with other efforts to limit pesticide build-up in the environment and to develop short-lived pesticides. It is important to appreciate that a very unstable nonpersistent pesticide could probably be held safely attached to, and protected by, the polymer matrix of the solid waste until released to do its work and then decompose.

At the University of Washington, work on this concept of controlled release solid waste pesticides has been underway for the past three years and the results are now presented in this report.

OBJECTIVES

The research was carried out in four discrete phases, each of which had a definite objective. These were:

Phase 1: Establish methods for chemically combining solid wastes with pesticides.

Phase 2: Demonstrate that solid waste-pesticide combinations have controlled release characteristics.

Phase 3: Develop and validate design theories for the prediction of the duration of effectiveness of controlled release combinations.

Phase 4: Field test the controlled release characteristics of solid waste-pesticide combinations.

Phase 1

Synthesis of Controlled Release Solid Waste Herbicide Combinations

In the establishment of methods for chemically combining solid wastes with pesticides, it was decided that herbicides should be explored first because of their extensive use in agricultural, horticultural, and industrial situations as well as in range and forest management.

Since sawdust, bark, and lignin all contain hydroxyl groups[92] and the more important herbicides are carboxylic acids,[93] the most obvious means of achieving their chemical combination would be by esterification. The formation of esters of cellulose[94] and lignin[95] as depicted in Eq. 1 is well known, and acid chlorides are easily prepared from the herbicides listed in Table III.

TABLE III

COMPOSITION OF HERBICIDE-FOREST SOLID WASTE COMBINATIONS[a]

Herbicide	*Forest solid waste*	*Herbicide content,[b] %*
2,4-Dichlorophenoxyacetic acid (2,4-D)	Bark	5.3, 12.3, 19.7, 27.4, 34.7
	Cellulose	7.3, 15.3, 17.5, 24.2, 31.8
	Kraft lignin	15.1, 21.8, 39.0
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	Bark	17.5, 23.8
	Cellulose	28.6, 38.1
	Kraft lignin	37.5, 50.0
4-(2,4-Dichlorophenoxy)butyric acid (2,4-DB)	Bark	20.8, 30.9, 36.8, 50.0
	Kraft lignin	29.5, 39.3
4-(2,4,5-Trichlorophenoxy)butyric acid (2,4,5-TB)	Bark	11.5
	Kraft lignin	21.9
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	Bark	51.1
	Kraft lignin	23.0, 38.5
4-(2-Methyl-4-chlorophenoxy)butyric acid (MCPB)	Bark	8.2, 28.9, 43.9
	Kraft lignin	12.9, 41.8
Trichloroacetic acid (TCA)	Bark	17.9
	Kraft lignin	6.5, 9.7
	Sawdust	11.9
2,2-Dichloropropionic acid (dalapon)	Bark	20.4
	Kraft lignin	10.6
	Sawdust	13.7
4-Amino-3,5,6-trichloropicolinic acid (Tordon)	Bark	11.0
	Kraft lignin	7.6
	Sawdust	8.6
2-(2,4,5-Trichlorophenoxy)propionic acid (silvex)	Bark	8.9, 18.2, 30.9
	Kraft lignin	12.3, 28.2, 42.2

[a] In bioassays to be reported later all these combinations showed controlled-release herbicidal characteristics.

[b] Expressed as the weight of free herbicide liberatable by hydrolysis.

For lignin, homogenous esterification media can be readily obtained. However, for the other wood wastes, the reaction system must be heterogenous. In practice, the latter has several advantages, even for lignin. Thus, the problems of preparing, handling, and heating viscous polymer solutions are eliminated. Subsequent isolation of the modified polymer from solutions is also avoided, and moderately expensive solvents can be replaced by low-cost aromatic hydrocarbons. Moreover, the heterogenous reaction system should be applicable to a broad range of solid wastes and should be comparable in cost to the processes currently used to prepare the commercial esters of herbicide acids.

$$\left.\begin{matrix}\text{Sawdust}\\ \text{Bark}\\ \text{Lignin}\end{matrix}\right\}\text{OH} + \text{Herbicide-COCl} \rightarrow \left.\begin{matrix}\text{Sawdust}\\ \text{Bark}\\ \text{Lignin}\end{matrix}\right\}\text{OCO-Herbicide} + \text{HCl} \qquad (1)$$

The extent of esterification achieved with the solid waste depends upon the proportion of the reactants, but the combined herbicide-polymer weight ratios at maximum substitution are, of course, determined by the concentration of accessible hydroxyl groups in the polymeric substrate and by the molecular weight of the pesticide. Thus, for kraft lignin and 2,4-dichlorophenoxyacetic acid (2,4-D,MW = 221), for example, the maximum weight ratio is approximately 1:1 since the equivalent weight of the lignin is about 250.[95] Any further entrapment of the herbicide above this value is not attributable to ester linkages. Practical weight ratios of pesticide to polymer substrate are determined by the duration of protection needed for a particular application.

Confirmation of chemical combination of the herbicide with the substrate was secured by continuous exhaustive extraction with boiling

solvent in a Soxhlet apparatus (Table IV). Under these circumstances, almost all of the herbicide is unextractable. The small loss is due to the removal of free herbicide acid and solvent-soluble neutral low molecular weight esters. These were present in about equal amounts for the cases checked quantitatively.

The herbicide acid presumably originates from the hydrolysis of the acid chloride by adventitious water in the wood-derived substrate. For this reason, the substrate should be carefully dried to a low moisture content (<1%) before reaction. However, it is probably almost impossible to eliminate all traces of free water from the final product by pre-drying because during the reaction, labile hydroxyl groups in the substrate may split off to yield water. This free herbicide in the pesticide-polymer combination need not be disadvantageous, as it can provide the initial amount necessary to wipe out more mature and established weeds. The solid waste combination is itself, of course, biologically inactive and nonleachable because of its water insolubility. Thus, we have materials in hand in which solid wastes are chemically combined with herbicides.[96]

Phase 2

Evaluation of the Controlled Release Solid Waste Herbicide Combinations

The object of this phase of the program was to show whether particular solid waste herbicide combinations would release herbicide at controlled rates. In order to determine the rate of release, either the amount of loss of the combination or the amount of free herbicide must be measured at various times. Ideally this should be repeated, keeping all but one of the possible factors constant. However, the

TABLE IV

BENZENE EXTRACTABILITY OF HERBICIDE-FOREST SOLID WASTE COMBINATIONS

Herbicide – forest solid waste combination	*Herbicide content,[a] %*	
	Before extraction	*After extraction*
2,4-D/bark	19.7	17.3
2,4-D/bark	34.7	32.6
2,4,5-T/bark	23.8	21.2
2,4-DB/bark	32.0	30.0
2,4-D/kraft lignin	21.8	20.1
2,4,5-T/kraft lignin	37.5	35.9

[a] Expressed as the weight of free herbicide liberatable by hydrolysis.

volume of work that would be needed to carry out the many analyses required made this approach impractical.

It was therefore decided to evaluate the combinations in natural conditions and follow the release by a bioassay technique. Such bioassay procedures have been previously established for chlorophenoxy acids.[97-99] The plants used were alfalfa, cucumber, sorghum, lettuce, and radish. Lettuce seeds (Lactuca sativa L.) was chosen in this work because lettuce is very sensitive to 2,4-D and thus a low concentration of the pesticide could be detected. The lettuce seeds will only germinate at very low concentrations of 2,4-D and will cease to germinate in its presence. This approach avoids the complexities and uncertainties of measuring the inhibition of growth of shoots.

The length of time that lettuce seed would not germinate in soil mixed with a controlled release solid waste herbicide combination was considered to be the degree of protection provided by that particular combination.

The results from the soil evaluation show that combinations were more effective than the commercial herbicide alone. The results are shown diagrammatically in Fig. 1. The length of inhibition of germination (in days) is shown for each combination. The end of each horizontal line is the day when germination was first observed. This is noted for each initial concentration of the combination in the soil. This value is not given in terms of the weight of polymer solid waste combination but in the weight (mg) of the 2,4-D which it originally contained.

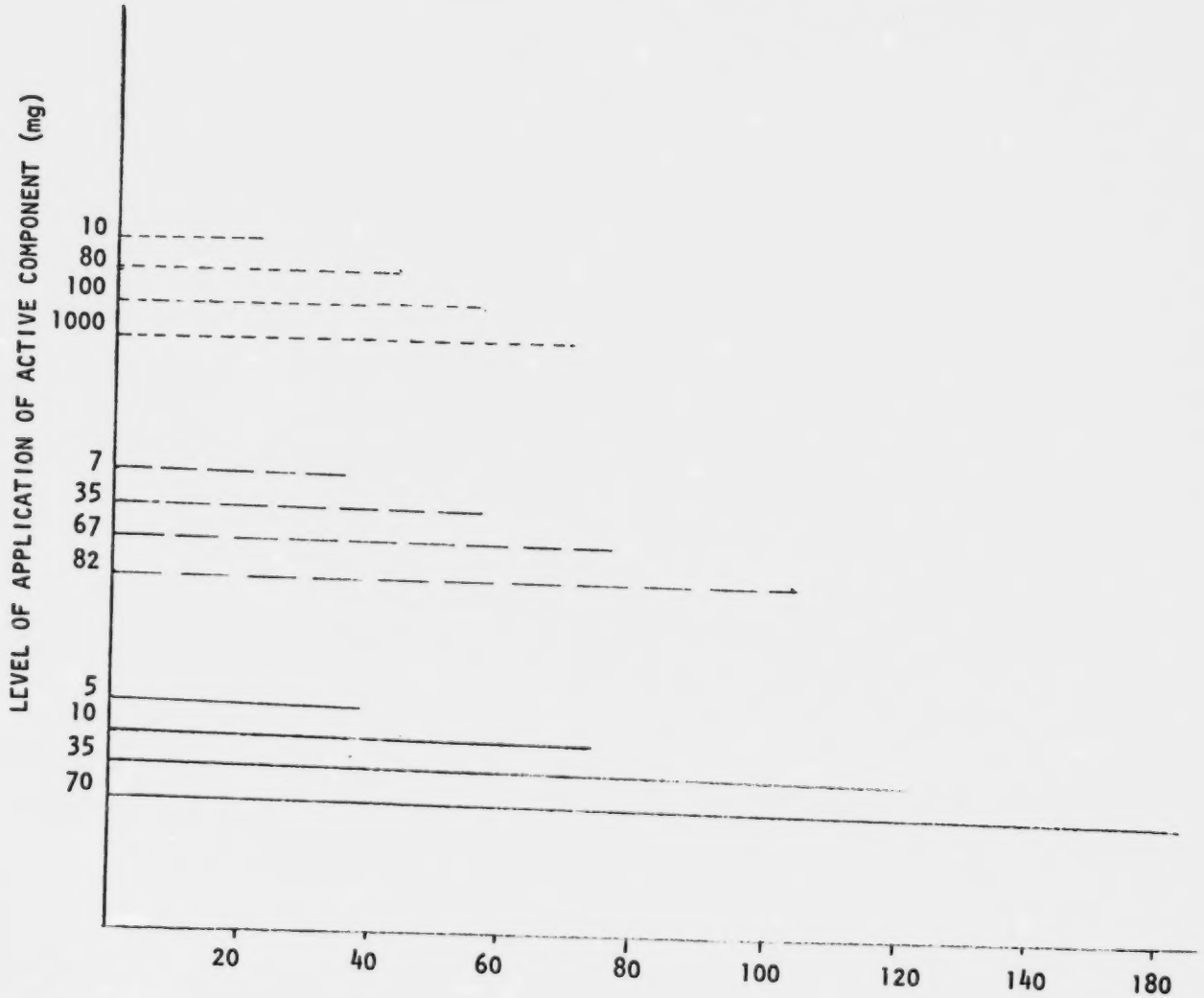

FIG. 1. DURATION OF HERBICIDAL EFFECTIVENESS (DAYS)

PERIOD OF PROTECTION OFFERED BY VARIOUS CONTROLLED RELEASE COMBINATIONS

--- 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D) ALONE;

– – 19.7% 2,4-D/DOUGLAS FIR BARK CHEMICAL COMBINATION;

—— 39.0% 2,4-D/KRAFT LIGNIN CHEMICAL COMBINATION

Phase 3

Development and Validation of Design Theories for Controlled Release Pesticides

After developing the methods for the synthesis of solid waste pesticide combinations and proving that they were biologically active, attention was directed to the establisnment and testing of theories for the prediction of the duration of effectiveness of controlled release combinations, where pesticide release occurs by degradation of a polymer containing the pesticide as a pendent side chain.[23] In this type of solid waste combination, the pesticide, exemplified by the herbicidal phenoxyacetic acids (RCOOH), is chemically attached as a pendent substituent to a natural or synthetic water-soluble or insoluble polymer having a replaceable hydrogen as formulated in equation (1). Obviously, the pesticide must also contain a structural moiety suitable for use as a link to the macromolecule,[22] and the carboxyl group is only one of the many alternatives possible.

$$\underset{(X = N,\ O \text{ or } S)}{\text{Polymer-X-H}} + \text{RCOOH} \overset{\text{synthesis}}{\underset{\text{environment}}{\rightleftharpoons}} \text{Polymer-X-COR} \qquad (1)$$

In the biological environment, side chain degradation occurs so that the chemical bonds holding the pesticide within its polymeric prison are sequentially broken to provide a sustained release of the pesticide over an extended period of time. The rate of release will clearly be determined by the nature of the pesticide-polymer bonds, the chemical characteristics of the pesticide and polymer and the dimensions and structure of the

resultant macromolecular combination. Where the polymeric backbone is water-soluble, the duration of pesticide release (D_{pr}) for n spherical particles (radius r and density ρ) of the pesticide-polymer combination in a water-saturated heterogeneous surface reaction is given by

$$D_{pr}=\rho r_o/k_h C_o-(R_h\rho^2/n\pi k_h{}^3 C_o{}^3) \qquad (2)$$

where C_o is the initial concentration of pesticide-polymer linkages on the surface of a particle of radius r_o, R_h is the rate of hydrolytic degradation and k_h is the hydrolysis rate constant. Since each pesticide molecule released by hydrolysis exposes another pesticide-polymer linkage beneath, C_o is a constant and the duration of pesticide release (D_{pr}) can be predicted from equation (3) in which

$$D_{pr} = A - BW^{-\frac{1}{3}} \qquad (3)$$

where A and B are constants and W is the amount of pesticide-polymer combination used. The validity of this equation is demonstrated by the linear plot (Fig. 2) of the persistence of herbicidal activity[23] exhibited by a polymer synthesized by the partial acylation (56.1%) of polyvinyl alcohol with 2-methyl-4-chlorophenoxyacetyl chloride. The duration of pesticide release was determined by observation of the inhibition by a herbicide of germination in lettuce seed sown daily. Equation (3) also defines the minimum amount of pesticide-polymer combination ($W = B^2/A^2$ when $D_{pr} = 0$) necessary for pesticidal activity.

On the other hand, the polymeric backbone selected may be water-insoluble and cellulose and lignin, the macromolecules of wood and bark,

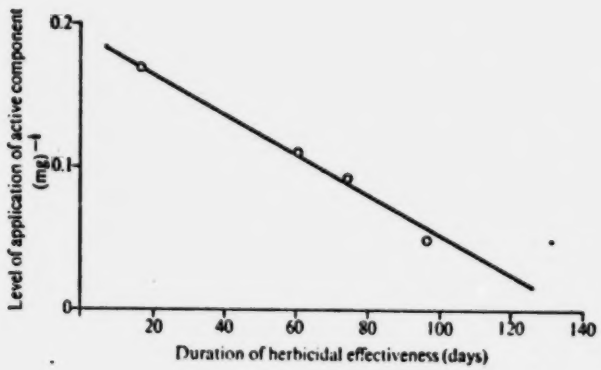

FIG. 2. RELATIONSHIP OF DURATION OF HERBICIDAL EFFECTIVENESS TO LEVEL OF APPLICATION FOR 2-METHYL-4-CHLOROPHENOXYACETIC ACID CHEMICALLY COMBINED WITH A WATER SOLUBLE POLYMER.

are particularly appropriate choices because of their long-established biodegradability and ecological acceptability and because of their abundance as low-cost solid wastes.[3] Marine[100] and proteinaceous[101] solid wastes can also be used as the polymeric backbone. Acylation of these natural hydroxylated polymers[102] with a pesticide acid chloride affords pesticide-polymer combinations which degrade by a heterogeneous surface reaction to provide a sustained release of pesticide.

The duration of effectiveness (D_{pr}) of this type of sustained release pesticide-polymer combination is given by

$$D_{pr} = (1/k_d)(\ln W - \ln R_d/k_d) \qquad (4)$$

where W is again the amount of pesticide-polymer combination used, R_d is the rate of degradation and k_d is the degradation rate constant.

Since k_d and R_d are constants for a given system, equation (4) can be simplified so that

$$D_{pr} = M \log_{10} W - N \qquad (5)$$

where M and N are constants. In this case, the minimum amount of pesticide-polymer combination necessary for pesticide activity is $10^{N/M}$ ($D_{pr} = 0$). Experimental confirmation of the usefulness of equation (5) in the design of controlled release pesticide-polymer combinations is again provided by the lettuce seed germination bioassay of the release of herbicide acids from esters of cellulose and lignin (Fig. 3).

The ecological implications of the behavior of all of these materials are perhaps their most important characteristic. The results in Fig. 3, for

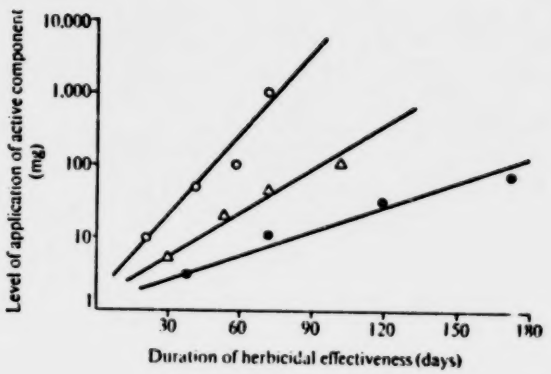

FIG. 3. RELATIONSHIP OF DURATION OF HERBICIDAL EFFECTIVENESS TO LEVEL OF APPLICATION FOR 2,4-DICHLOROPHENOXYACETIC ACID (2,4-D) CHEMICALLY COMBINED WITH WATER INSOLUBLE POLYMERS.

- o 2,4-D ALONE;
- Δ 19.7% 2,4-D/DOUGLAS FIR BARK CHEMICAL COMBINATION;
- ● 39% 2,4-D/KRAFT LIGNIN CHEMICAL COMBINATION.

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example, show that controlled release combinations in comparison with free pesticide provide either an extended period of protection at equivalent levels of application or the same period of protection at greatly reduced levels of application. Clearly, both of these alternatives tend to reduce the environmental hazards associated with the continued use of conventional pesticides.

Phase 4

Field Testing of Controlled Release Pesticides

With the completion of phases 1-3, the research program had reached the point, ahead of schedule, where field tests had to be implemented to advance the concept of solid waste reuse in controlled release pesticides. However, the number of applications which can be visualized for such combinations is immense and moreover the concept is broadly applicable to the release of other biologically active substances.

In the University of Washington program, it has been most appropriate to direct the major effort towards greenhouse and field testing of the theories developed in a forestry context, both in temperate and tropical regions. The problems tackled were as follows:

Selective Suppression of Weeds and Deciduous Brush in the Presence of Conifers. The reforestation of commercial forest land with conifers is retarded by fast-growing deciduous brush which in the Pacific Northwest is typified by western red alder (Alnus rubra Bong.) and vine maple (Acer circinatum Pursh.). These deciduous plants, and their counterparts elsewhere regionally, tend to crowd and overshadow the conifers during their first five to ten years of growth and provide root competition for water and nutrients for many further

years. The adverse influence of deciduous brush is, of course, not limited to competitive effects. Other identified liabilities associated with thick brush are (a) intensification of ground heat with concomitant increased conifer transpiration stress, (b) augmented rodent populations that girdle and clip seedlings and may consume costly planted seeds in adjoining areas, and (c) the matting of gymnosperms under heavy accumulations of fallen leaves and other dead materials.[103]

In spite of the recognition of this brush problem, however, its control by herbicide application is far from straightforward from both a technical and economic viewpoint. Technically, for example, total elimination of the brush might force wildlife to forage more intensively on the tree crop, and deer grazing on the luscious leaders of seedlings is already a most serious source of damage in the tree farms of the Northwest.[104,105] Moreover, it has been demonstrated[106] that moderate weed control (60% average) over a two-year period was sufficient to ensure optimal growth of two-year-old seedlings of both white spruce (Picea gluca [Moench] Voss) and Colorado spruce (Picea pungens Engelm.). Nonetheless, even the attainment of this modest degree of brush control has been fraught with difficulties, because commercially available herbicides are not clearly selectively toxic to brush and non-toxic to conifers. The most promising materials, according to the work of Rediske and Staebler[107] are the chlorophenoxybutyric acids and these auxin-like herbicides have no adverse ecological effect on the quantity or activity of the micro-organisms in the soil.[108-110] Moreover, in field tests the triethylamine salt of 2,4-dichlorophenoxybutyric acid reduced the density of canopies of mixed western red alder and vine maple. Unfortunately, however, these butyric acid herbicides can readily be oxidized in the soil to the corresponding chlorophenoxyacetic acids and these are much

more toxic to conifers.[107] Excessive loss or damage of seedlings can then easily occur. Furthermore, it is also clear that the general and indiscriminate spraying of large areas of forest lands is costly and inefficient, especially if multiple treatments are required. Helicopter application, for example, costs about $10 per acre in the Pacific Northwest. In addition, in view of the areas involved, such aerial blanketing of forest lands with herbicides may be ecologically undesirable, particularly for 2,4,5-trichlorophenoxy-γ-butyric acid because the derived 2,4,5-trichlorophenoxyacetic acid has considerable persistency[6] which by runoff could ultimately invite water pollution problems.[5,111]

To solve this forest pest management problem, a greenhouse study was undertaken to determine the level of controlled release combinations of 2,4-DB with bark which would be phytotoxic to unwanted deciduous brush Western alder (Alnus rubra, Bong.) and nontoxic to Douglas-fir (Pseudotsuga menziesii [Mirb.] Franco).

The data in Table V[112] showing the complete crown kill of western red alder seedlings demonstrates that all of the chemical combinations of 2,4-dichlorophenoxybutyric acid with Douglas-fir bark are indeed biologically active at every level of application. At all levels used the first signs of phytotoxicity were observed 25 days after the application of the controlled release combination and the crowns were completely dead within a further 110 days. This activity was also exhibited towards the Douglas-fir seedlings but only at the higher levels of application where initial damage became apparent 45 days after treatment. The realization of crown kill was also more sluggish for the softwood seedlings, and 205 days elapsed before the seedlings expired. The differentiation of the controlled release herbicide between the gymnosperm and angiosperm seedlings was

TABLE V

EXTENT OF CROWN KILL IN DOUGLAS-FIR AND WESTERN RED ALDER SEEDLINGS TREATED WITH CHEMICAL COMBINATIONS OF 2,4-DICHLOROPHENOXYBUTYRIC ACID AND DOUGLAS-FIR BARK

Amount of herbicide-bark combination applied	Releasable herbicide content	Average height of transplanted seedling at time of treatment		Extent of crown kill	
		Douglas fir	w. red Alder	Douglas fir	w. red Alder
10g	50%	25cm	37cm	0%	100%
55	50	26	38	100	100
100	50	25	38	100	100
10	37	26	38	0	100
55	37	24	37	100	100
100	37	25	38	100	100
10	31	30	46	0	75
55	31	32	47	75	100
100	31	31	45	100	100

greatly enhanced at the lower levels of application (10g) when the Douglas-fir seedlings were unharmed while the western red alder seedlings succumbed. This, of course, implies that a herbicidal combination selectively phytotoxic to deciduous species may now be in hand.

This conclusion is supported by the measurements of seedling heights collected in Table VI, which show that the controlled release combinations do not adversely affect the growth of the Douglas-fir seedlings in any way.

The data in Table VI[112] also illustrate the vigorous growth of western red alder during one growing season. Percentage height increases of 68-80% were recorded, and it is clear that the water and nutrients necessary to generate this hardwood biomass would be more profitably utilized in augmenting the growth of the desired softwood. Moreover, the root competition in reforestation provided by hardwoods is supplemented by other vegetation which also consumes nutrients and water. The magnitude of this additional adverse factor to softwood growth is indicated by quantity of vegetation growing around the seedlings which have not been treated with the controlled release herbicide-bark combination. This biomass was measured by weight and after one growing season, averaged about 7g around the softwood seedlings and about 12g around the hardwood plants (Table VII). Thus, both the untreated Douglas-fir and western red alder seedlings are much more weed-infested than the seedlings treated with the controlled release herbicide-bark combinations. Those treated pots are essentially devoid of weeds at all levels of application and this demonstrates clearly that the germination of weed seeds is inhibited by the herbicidal bark combination over the entire growing season. This could be of particular importance in conifer stand establishment because Grover has shown that

TABLE VI

EXTENT OF HEIGHT INCREASE OF DOUGLAS-FIR AND WESTERN RED ALDER SEEDLINGS TREATED WITH CHEMICAL COMBINATIONS OF 2,4-DICHLOROPHENOXYBUTYRIC ACID AND DOUGLAS-FIR BARK, AFTER ONE GROWING SEASON

Amount of herbicide-bark combination applied	Releasable herbicide content	Height Increase for Douglas fir		Height Increase for Western Red Alder	
		Untreated	Treated	Untreated	Treated
10g	50%	55%	54%	80%	0%
10g	37%	54%	56%	78%	0%
10g	31%	49%	50%	68%	16%

TABLE VII

EXTENT OF ROOT COMPETITION (VEGETATION YIELD) AROUND DOUGLAS-FIR AND WESTERN RED ALDER SEEDLINGS TREATED WITH CHEMICAL COMBINATIONS OF 2,4-DICHLOROPHENOXYBUTYRIC ACID AND DOUGLAS-FIR BARK, AFTER ONE GROWING SEASON

Amount of herbicide-bark combination applied	Releasable herbicide content	Vegetation yield around			
		Douglas fir		Western red alder	
		Untreated	Treated	Untreated	Treated
10g	50%	8g	0g	17g	0g
55	50	10	0	10	0
100	50	6	0	17	0
10	37	10	0	15	0·2
55	37	7	0	12	0
100	37	5	0	10	0
10	31	6	0·1	9	0·2
55	31	5	0	8	0
100	31	6	0	11	0

significant reductions in the growth of transplants occur as a result of competition from weeds present during the first two years of growth.[106]

The selectivity of the chemical combinations of 2,4-dichlorophenoxybutyric acid with Douglas-fir bark is a consequence of two factors; the structure of the herbicide and its rate of release into the ecosystem. Thus, it is well established[107,110] that the butyric acids with γ-substituents exemplified by 2,4-dichlorophenoxy, 2,4,5-trichlorophenoxy, and 4-chloro-2-methylphenoxy, unlike the corresponding acetic acids, are not herbicidal. The apparent herbicidal activity observed is a consequence of the *in vivo* conversion of the inactive butyric acids into the corresponding active acetic acids by those species possessing an appropriate β-oxidizing enzyme system.[113-115] Western red alder almost certainly contains such a β-oxidase because a leaf homogenate on admixture with triethylammonium 2,4-dichlorophenoxybutyrate proved toxic to Douglas-fir seedlings[107] while the herbicide alone was without effect because the conifers do not contain a β-oxidase. Of course, the forest floor must also contain some β-oxidases originating from fallen leaves. This means that a bulk application of a butyric acid herbicide cannot be used as a selective treatment because it will soon be transformed in the soil into a mixture of the applied butyric acid herbicide selective to deciduous brush and the analogous nonselective acetic acid derivative. This situation is avoided by the use of a chemical combination of the butyric acid with the polymeric components of bark. The ester linkage joining the herbicide to the bark will not be easily attacked by any β-oxidase and the butyric acid herbicide is thereby stabilized. Essentially, the only butyric acid herbicide available for β-oxidation is that continuously being released from the bark. This release will occur whether the combination lies in or on the surface of the soil since attack

by moisture, micro-organisms and the weather can occur in either of these zones. However, as the butyric acid escapes from its chemical incarceration, absorption by plants will be competitive with attack by the β-oxidizing enzyme system in the soil. Since the former is a simple physical diffusional phenomenon in contrast to the complex physical and biochemical processes prerequisite to oxidation, it can be assumed that absorption of the butyric herbicide will be faster than its oxidation to the phytotoxic acetic acid counterpart. A satisfying explanation of the selective phytotoxicity of the controlled release combination of 2,4-dichlorophenoxy-γ-butyric acid with bark is thereby provided.

Selective Suppression of Weeds and Deciduous Brush in the Presence of Douglas-Fir Seedlings in an Area of Medium Rainfall. A selective herbicidal material potentially useful in conifer stand establishment therefore now appeared to be available as a result of this research. At this stage, it was essential that controlled release bark/2,4-DB combinations should be tried under field conditions. This was achieved with the cooperation of the Department of Natural Resources of the State of Washington. The site selected for this purpose, Muddy Creek, is located near Sedro Woolley, Washington. The site was logged in the winter of 1969 and was burned in August, 1970. Nursery stock Douglas-fir seedlings, 2-3 year old, were transplanted in January, 1971. In April, 1971, these seedlings were treated with bark/2,4-DB combinations at several different levels.

After one growing season all levels of treatment of controlled release bark/2,4-DB combinations showed no phytotoxic effect on the Douglas-fir seedlings but these levels did cause damage to the surrounding weeds and deciduous brush. The results also indicate that there are no ill effects on the growth rate of treated seedlings (Table VIII) but on the contrary,

TABLE VIII

MUDDY CREEK FIELD TRIALS

COMPARISON OF GROWTH INCREMENT OF UNTREATED DOUGLAS-FIR SEEDLINGS IN A PLOT* OF DOUGLAS-FIR SEEDLINGS TREATED WITH A CONTROLLED RELEASE COMBINATION** OF 2,4-DICHLOROPHENOXYBUTYRIC ACID AND DOUGLAS-FIR BARK, AFTER ONE GROWING SEASON

Plot Designation	Amount of Herbicide-Bark Combination Applied to Treated Seedlings	Average Height of Seedlings in the Months, 1971				Height Increase for Seedlings	
		March		September			
		Treated	Untreated	Treated	Untreated	Treated	Untreated
E	200g	44cm	37cm	62cm	48cm	41%	30%
J	200	41	41	61	51	49	24
B	500	43	39	58	49	35	26
L	500	48	39	67	50	40	28
A	1250	50	39	71	46	42	18
T	1250	48	40	66	49	38	22
M	2000	45	41	67	52	49	27
R	2000	66	42	59	52	34	24
D	0	38	--	45	--	18	--
F	0	42	--	54	--	29	--
P	0	40	--	49	--	22	--

** The combination contains 37% of releasable herbicide

* In each plot of 32 seedlings, 16 were treated with the controlled release herbicide

combinations enhance the percentage height increase, up to 49% as compared to 18% for the untreated seedlings (Table VIII). Vegetation cover on the scale of 0-10 is suppressed from 8 to 1 in the case of the treated seedlings (Table IX).

These results are extremely important for reforestation as there is an increased probability that all of the planted seedlings may survive because of the reduced competition. Furthermore, the solid waste combinations reduce weeds which can adversely affect the growth rate of the fir seedlings and can also act as a cover for animals such as deer[104,105] which may severely damage the fir crop. However, at the same time, there would be enough vegetation remaining available as forage for these animals; ecologically and aesthetically, this vegetation is essential.

It has been noted[116] that in some cases less than 30% of the pesticides applied reach the target with the rest going to nontarget organisms and causing havoc to other crops as well as air and water pollution.[117] To study possible herbicide migration in this field test, fir seedlings adjacent to treated areas were studied carefully but no phytotoxic effect was observed. The height increases observed are closer to the untreated controls than to the treated seedlings (Table VIII). Vegetation levels (Table IX) in the adjacent areas also confirm that no migration of herbicide occurred.

This study showed that there is no necessity of broadcasting the pesticides in the reforestation programs and only 1/8th of the total area need be treated with controlled release combinations. This implies that dissemination of pesticides in the environment could be greatly reduced and this method of application may be lower in cost. Thus, these results have established that the concept of reusing wood-derived waste by the chemical attachment of herbicides is practical in reforestation programs.

TABLE IX

MUDDY CREEK FIELD TRIALS

COMPARISON OF ROOT COMPETITION AROUND UNTREATED DOUGLAS-FIR SEEDLINGS AND UNTREATED DOUGLAS-FIR SEEDLINGS IN A PLOT OF DOUGLAS-FIR SEEDLINGS TREATED WITH A CONTROLLED RELEASE COMBINATION** OF 2,4-DICHLOROPHENOXYBUTYRIC ACID AND DOUGLAS-FIR BARK, AFTER ONE GROWING SEASON

Plot No.	Amount of Herbicide-Bark Combination Applied	Vegetation Yield* Around Douglas Fir Seedlings		
		Untreated Outside Plot	Untreated In Plot	Treated
E	200g	7	5	3
J	200	7	6	5
B	500	8	5	3
L	500	6	5	2
A	1250	8	5	4
T	1250	6	3	1
M	2000	8	4	2
R	2000	6	3	2

** The combination contains 37% of releasable herbicide

* In each plot of 32 seedlings, 16 were treated with the controlled release herbicide

However, the validating field demonstration was modest in scope and was conducted at only one location. It was therefore extremely important that more field trials should be conducted in other locations having different climatic conditions. This has been achieved with the cooperation of the State of Washington Department of Natural Resources which supplied the trees, land, labor, and equipment at several sites within the State of Washington. These field trials are:

Suppression of Weeds and Deciduous Brush in the Presence of Douglas-Fir Seedlings in an Area of Light Rainfall. This field trial was established at Glenwood (Site 1) to examine the following parameters: (1) the minimum level of application necessary to achieve selective toxicity to the unwanted vegetation, (2) the effect of broadcast vs. localized treatment of the test area, (3) the relationship of the annual rainfall of the area on the release rate of the bark-herbicide combinations, and (4) the maximum amount of solid waste which can be utilized by this technology.

The test site which was clearcut in 1957-58 was bulldozed and planted with 1-2 year old Douglas-fir seedlings on March 15, 1972. The 1/2 acre site was divided into twelve plots, each containing 30-35 seedlings. Twenty seedlings in each plot were treated on May 19, 1972, with controlled release bark-herbicide (2,4-DB) combinations. The average annual rainfall in this area is less than 30 inches.

Suppression of Weeds and Deciduous Brush in the Presence of Ponderosa Pine Seedlings in an Area of Light Rainfall. Ponderosa pine is an important conifer in the drier areas of the State of Washington and the Department of Natural Resources suggested that the efficacy of the solid waste herbicide combination be checked out on this species. Site 2 was also selected in the Glenwood area.

It was 1/4 acre in size and was infested with deciduous brush. This was bulldozed and planted with 2-3 year old Ponderosa Pine seedlings on March 15, 1972. The area was subdivided into eight plots each containing 25-30 seedlings. On May 1, 1972, 20 seedlings in each plot were treated with different amounts of controlled release solid waste herbicide (2,4-DB) combinations. The annual rainfall in this area is below 30 inches.

Selective Suppression of Weeds and Deciduous Brush in the Presence of Douglas-Fir Seedlings in an Area of Heavy Rainfall. This site at Montesano was logged and slash burned on February 1, 1971, and it was planted with 1 year old Douglas-fir seedlings spaced 10'-10'. The tract used consists of about 1 acre on gently sloping ground and on the top of a hill which receives an annual rainfall of 60-80 inches. Vegetation common to this area include red alder, ferns, wild grass, thistle, and blackberries. On March 17, 1972, the one-acre tract was divided into 20 plots and all trees were labeled and their heights recorded. Then on May 17, 1972, 16 plots were treated with solid waste herbicide combinations and 4 plots were left untreated for use as controls.

The suppression of vegetation is also being investigated in field trials involving the application of controlled release herbicides on railroads, firebreaks, and powerline right-of-ways. The railroad and firebreak areas are again of vital interest to the Department of Natural Resources of the State of Washington and the land, facilities, and equipment were again provided by this agency. The powerline right-of-way was made available by the Puget Power and Light Company of Seattle. The field trials were initiated as follows:

Suppression of Vegetation in Railroad Right-of-Way . This is a screening experiment of various controlled release solid waste herbicide combinations

intended for the complete suppression of all vegetation. Near Thurston, Washington, the railroad right-of-way and a 12' x 825' area adjacent to the railway tracks was infested with wild grass, Canadian thistle, dandelions, and wild blackberries. Vegetation was plowed under on May 2, 1972, and the area was subdivided into twenty-two 12' x 31' plots with a 6'-wide buffer zone between each plot. On June 8, 1972, several controlled release herbicide combinations were applied to these plots at various levels.

Suppression of Vegetation Under a Powerline. This field trial near Kirkland, Washington, was designed to test the applicability of controlled release herbicide bark combinations for the control of brush beneath powerlines. The area (1/2 acre) chosen for this test is located near the town of Kirkland, Washington. Before the experiment was undertaken, the area had a dense plant population consisting of red alder, vine maple, scotch broom and many other wild species. The experimental area was cleared of brush, scraped to bare soil and divided into 400 square ft. plots separated from each other by buffer zones. On March 31, 1972, herbicide bark combinations were applied to 12 plots and 6 plots were used as controls with no herbicidal treatment.

Controlled Release Insecticides for the Protection of Mahogany and Cedar Against the Shootborer, *Hypsipyla grandella*, Zeller. With the successful field demonstration of a controlled release herbicide, attention was focused on the possibility of a similar demonstration in the insecticide area. Insects are, of course, a tremendous problem in the U.S. and the methods of control are ecologically poor. However, it is difficult to time the study of insecticides in the U.S. because the insects go through relatively few life cycles in a year. For this reason, it is preferable to conduct insect research in the tropics where the fecundity of insect life ensures a more or less constant pressure on any insecticide protection. Since the College of Forest Resources was

already involved in an entomological study of tropical forest insects, the stage was set for rapid progress. The particular insect problem tackled was the control of the shootborer, Hypsipyla grandella Zeller which attacks trees of the Meliaceae family such as mahogany and Spanish Cedar. Control of H. grandella by insecticides has been suggested,[118] but chemical treatments are considered too costly. The high cost is due to the short life cycle and overlapping generations of the pest, which in turn, call for repeated applications of insecticides to reduce damage to economically tolerable levels. Because of the short residual life of the more effective insecticides, especially in tropical climates with high rainfall, and because of the relatively long period during which Meliaceae trees must be protected, many investigators feel that biological or silvicultural remedies are indicated.[119-121] So to use systemic insecticides effectively, particularly in tropical climates where the average daily temperature is in the 80's and 90's and the yearly rainfall is well over 100 inches, two conditions are required. The first is a method of localized application to each plant and the second is a method of releasing the pesticide in quantities just sufficient to maintain protection. These conditions could be appropriately met by the controlled release combinations.

As no information was available in the literature regarding the insecticides suitable for the control of H. grandella, it was necessary to screen a number of known systemic insecticides (Table X) for effectiveness. This was carried out in the greenhouse of the Inter-American Institute of Agricultural Sciences at Turrialba, Costa Rica, by applying the insecticides (75mg) to the soil of the potted seedlings. The screening was carried out in two stages because of a shortage of Hypsipyla larvae due to a lack of host trees. The concentration of insecticide in the leaves of the treated

TABLE X

INSECTICIDES EVALUATED FOR THE CONTROL OF HYPSIPYLA GRANDELLA ZELLER

Common Names	Chemical Names
aminocarb	3-methyl-4-dimethylaminophenyl N-methylcarbamate
arprocarb	2-*iso*propoxyphenyl N-methylcarbamate
Bay 68138	ethyl 3-methyl-4-methylthiophenyl *iso*propyl phosphoramidate
carbofuran	2,3-dihydro-2,2-dimethylbenzofuran-7-yl N-methylcarbamate
Cyolane	2-(diethoxyphosphinylimino)-1,3-dithiolane
Cytrolane	2-(diethoxyphosphinylimino)-4-methyl-1,3-dithiolane
C-2307	3-(dimethylphosphinyloxy)-N-methoxy-N-methyl*cis*crotonamide
demeton	2:1 mixture of 0,0-diethyl 0- and S-2-(ethylthio)ethyl phosphorodithioate
dicrotophos	3-(dimethylphosphinyloxy)-N,N-dimethyl*cis*crotonamide
dimethoate	0,0-dimethyl S-(N-methylcarbamoylmethyl) phosphorodithioate
dimetilan	2-dimethylcarbamyl-3-methyl-5-pyrazolyl dimethylcarbamate
disulfoton	0,0-diethyl S-2-(ethylthio)ethyl phosphorodithioate
fenchlorphos	0,0-dimethyl 0-(2,4,5-trichlorophenyl) phosphorothioate
fensulfothion	0,0-diethyl 0-4-methylsulfinylphenyl phosphorothioate
fenthion	0,0-dimethyl 0-3-methyl-4-methylthiophenyl phosphorothioate
I-19	hexamethylditin
Isolan	1-*iso*propyl-3-methyl-5-pyrazolyl dimethylcarbamate
menazon	0,0-dimethyl S-(4,6-diamino-1,3,5-triazin-2-ylmethyl) phosphorodithioate
methomyl	S-methyl N-[(methylcarbamoyl)oxy] thioacetimidate
I-12	S-(N-methoxycarbonyl-N-methylcarbamoylmethyl)dimethyl phosphorothiolthionate
Monitor	0,S-dimethyl phosphoramidothioate
monocrotophos	3-(dimethoxyphosphinyloxy)-N-methyl*cis*crotonamide
oxydemeton-methyl	0,0-dimethyl S-2-(ethylsulfinyl)ethyl phosphorothioate
phorate	0,0-diethyl S-ethylthiomethyl phosphorodithioate
phosphamidon	2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate
Pirimor	5,6-dimethyl-2-dimethylamino-4-pyrimidinyl dimethylcarbamate
schradan	octamethylpyrophosphoramide
trichlorofon	dimethyl 2,2,2-trichloro-1-hydroxyethyl phosphonate

plants was followed by bioassay with Drosophila fruit flies. By this means, the time when each insecticide was at a maximum concentration was found. Collected Hypsipyla eggs were then attached to the leaves of other soil treated plants so that hatching occurred when the concentrations of the insecticides were at their respective maxima. The results of the effect of the presence of each insecticide on the insect were observed a week later.

Insecticides that protected the plant best under these conditions were carbofuran, methomyl, isolan, monocrotophos, phosphamidon, dimethoate, and Cytrolane,[122] (Fig. 4-6). As a prelude to developing controlled release forms of these chemicals, their phytotoxicity to seedlings had to be measured. This was carried out in a series of soil application experiments and carbofuran, methomyl, phosphamidon, and monocrotophos were found to provide the best combinations of control and lack of phytotoxicity (Fig. 7).

Although the free insecticides had shown the ability to provide protection in the moderate conditions of the greenhouse evaluation, it was not established that the same protection would be effective in the field because of the complexity of the tropical micro- and macro-environment. Moreover, the attachment of such complex insecticides to solid waste is an intricate problem in chemical synthesis. It was therefore decided to first determine, in a preliminary field trial, the effectiveness of a physical controlled release combination. The physical release concept is a subvariant of the broad controlled release concept in which the pesticide is embedded, encapsulated, or dissolved within a polymeric matrix. Controlled release is obtained by diffusion of the pesticide from the polymeric medium. This technique does not require the presence of any "chemical handle" on the pesticide. It was anticipated that once successful control of the shootborer had been obtained and the final choice of insecticide made, attention could be concentrated on chemical attachment to a solid waste substrate.

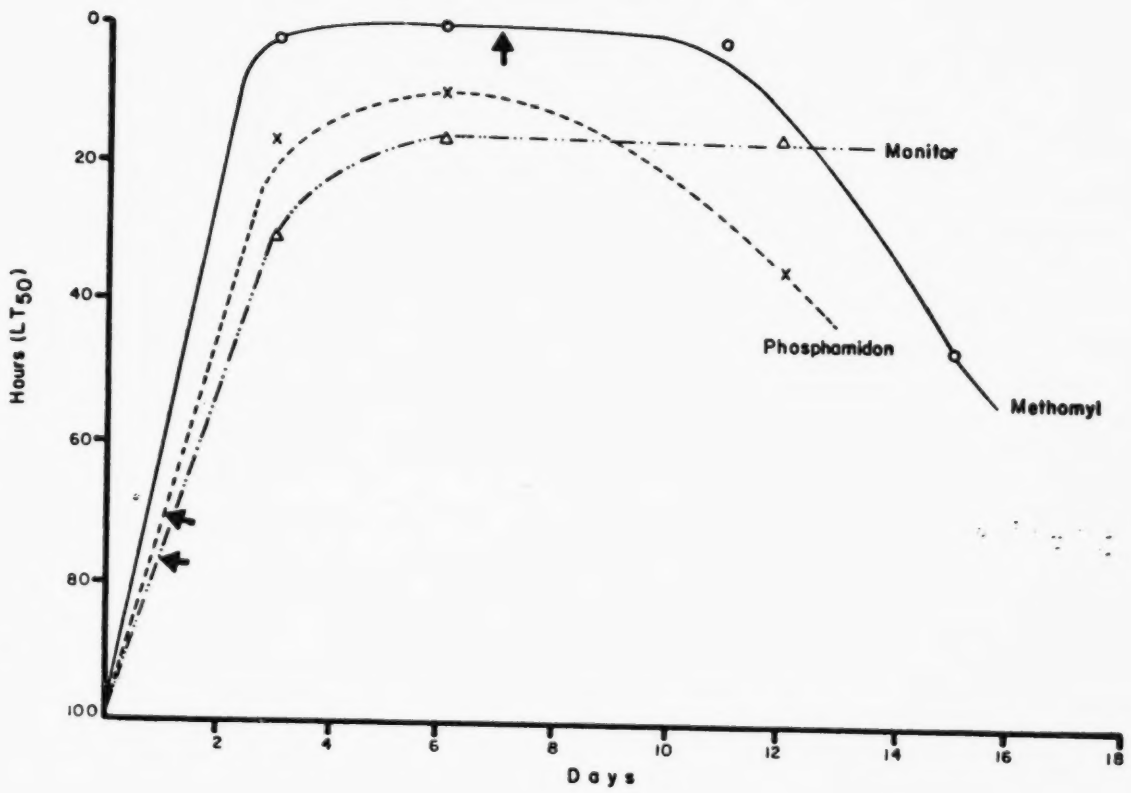

FIG. 4. CHARACTERISTIC CURVES OF "SYSTEMICITY" FOR PHOSPHAMIDON, MONITOR AND METHOMYL IN C. ODORATA. THE ARROWS INDICATE THE TIME OF ATTACHMENT OF H. GRANDELLA EGGS TO THE YOUNG TREES. ATTACK OCCURRED GENERALLY ABOUT 2 DAYS LATER.

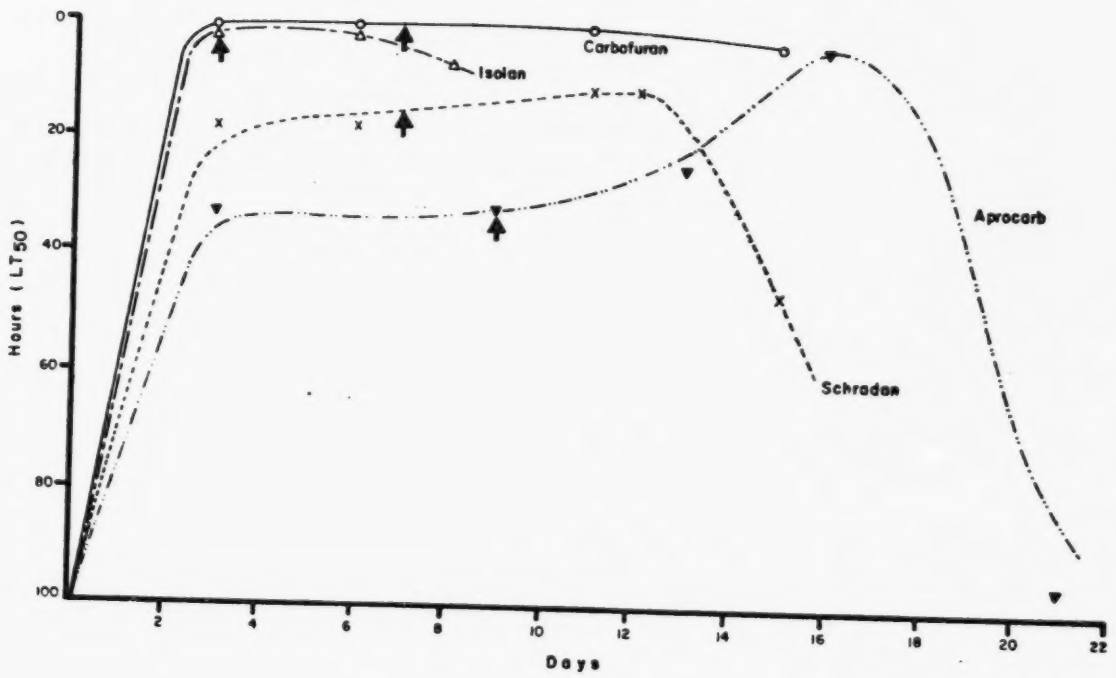

FIG. 5. CHARACTERISTICS CURVES OF "SYSTEMICITY" FOR CARBOFURAN, ARPROCARB ISOLAN AND SCHRADAN IN C. ODORATA.

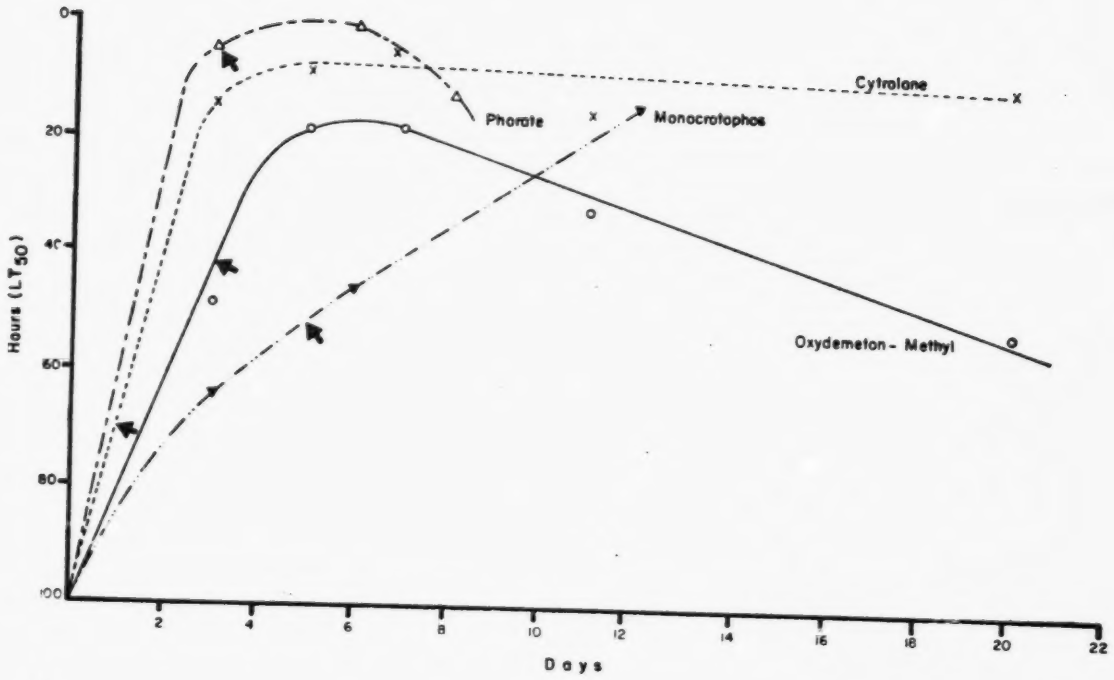

FIG. 6. CHARACTERISTIC CURVES OF "SYSTEMICITY" OF PHORATE, CYTROLANE, MONOCROTOPHOS AND OXYDEMETON-METHYL IN C. ODORATA.

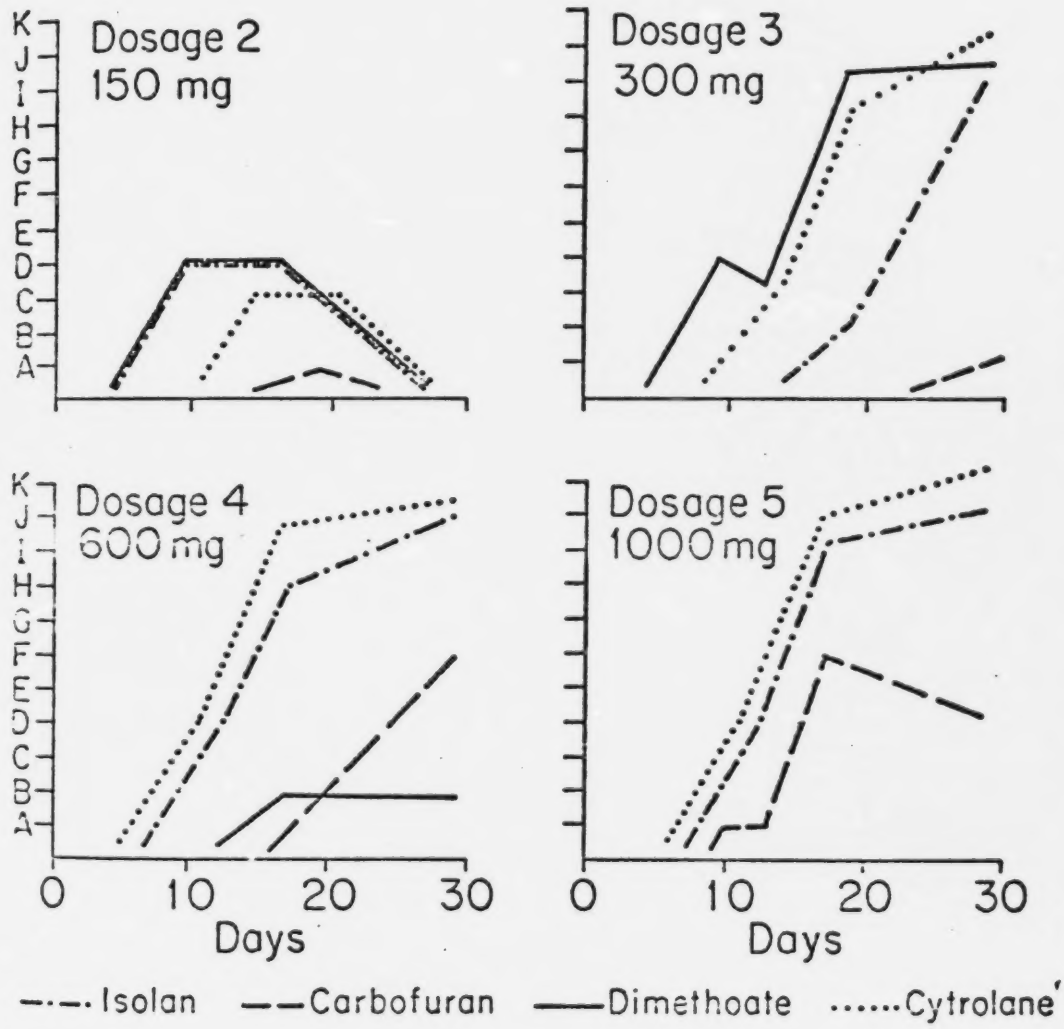

FIG. 7. PHYTOTOXIC EFFECT OF INSECTICIDES BY SOIL APPLICATION ON C. ODORATA

Controlled release formulations of the five most promising insecticides (carbofuran, methomyl, monocrotophos, Isolan, and phosphamidon) were therefore prepared by dissolution in a molten fatty polyamide resin and casting into cylindrical pellets. Sustained release of the insecticides was then obtained from diffusion through the polymeric matrix. The solid polymer pesticide solutions (containing 25% active ingredient) were field tested in plantations of C. odorata seedlings at two locations, Puente Cajon and Florencia Sur, near Turrialba, Costa Rica.

The young trees were treated with the same number of controlled release pellets (12) by placement in the soil around the stem. Other trees were soil treated with conventional formulations or were untreated. Observations of subsequent shootborer attack (Fig. 8-11) and average height of the trees (Fig. 12, 13) coupled with chemical analysis of insecticide residues in the leaves (Table XI) and pellets (Table XII) indicated the performance of the five insecticide-polymer combinations. The results of attack observations indicated that the periods of protection obtained with the controlled release formulations of Isolan, monocrotophos, and phosphamidon (about 90 days) and of methomyl (about 140 days) were longer than for the uncombined formulations (less than 30 days). The carbofuran combination gave almost complete control for a period of 340 days.

None of the controlled release insecticide formulations at the level used caused any serious acute or chronic phytotoxicity.

When determined 18 months after establishment of the plantations, the tree heights were maximum (Table XIII, XIV) and shootborer damage was minimal (Table XV, XVI) for trees treated with the carbofuran pellets. All controlled release insecticide treated trees were higher on the average than untreated trees at time.

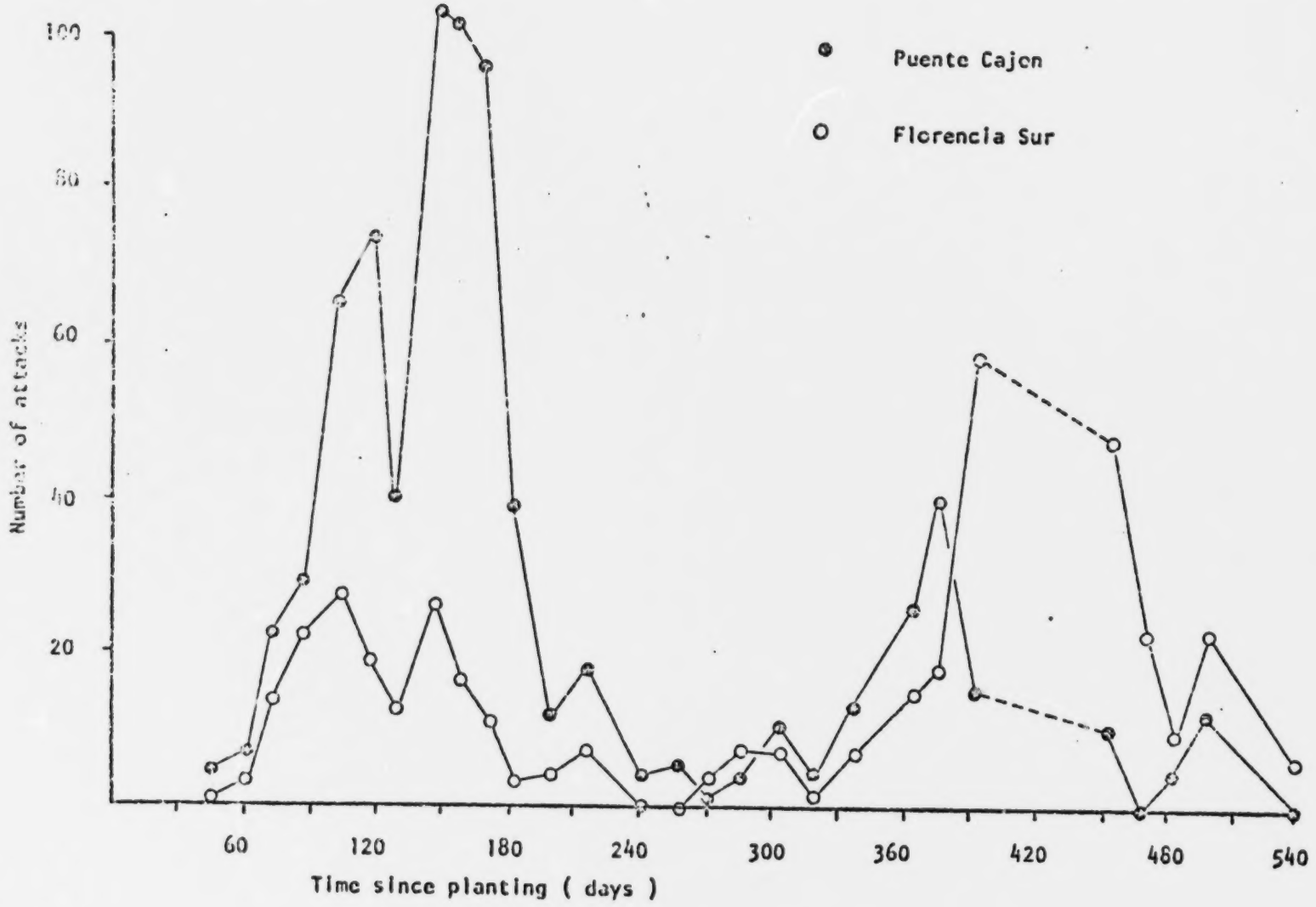

FIG. 8. THE FREQUENCY OF ATTACKS IN THE PLANTATIONS AT PUENTE CAJON AND FLORENCIA SUR.

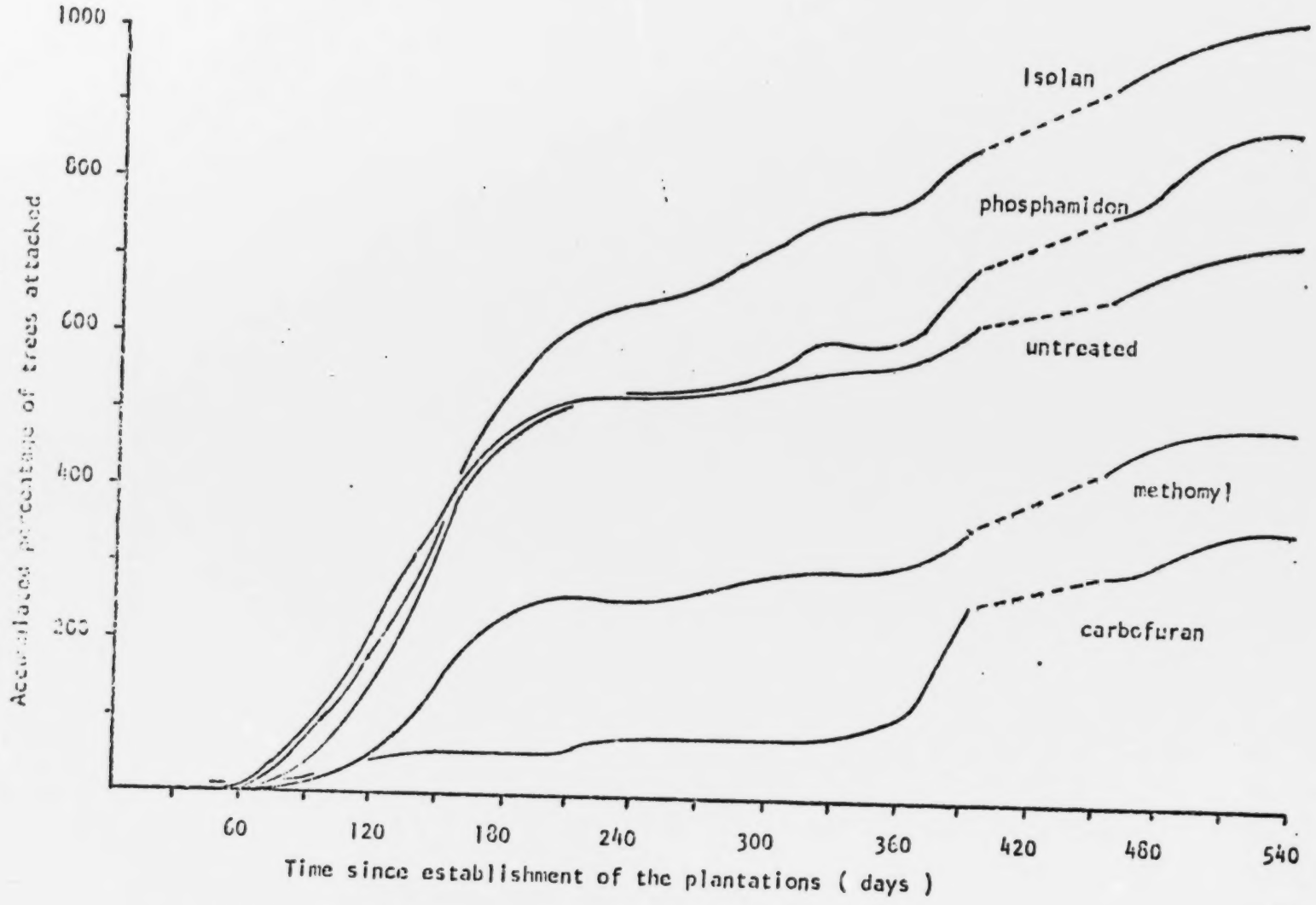

FIG. 9. FREQUENCY OF ATTACKS FOR EACH TREATMENT GROUP, EXPRESSED AS THE PERCENTAGE OF TREES ATTACKED, FOR BOTH PLANTATIONS.

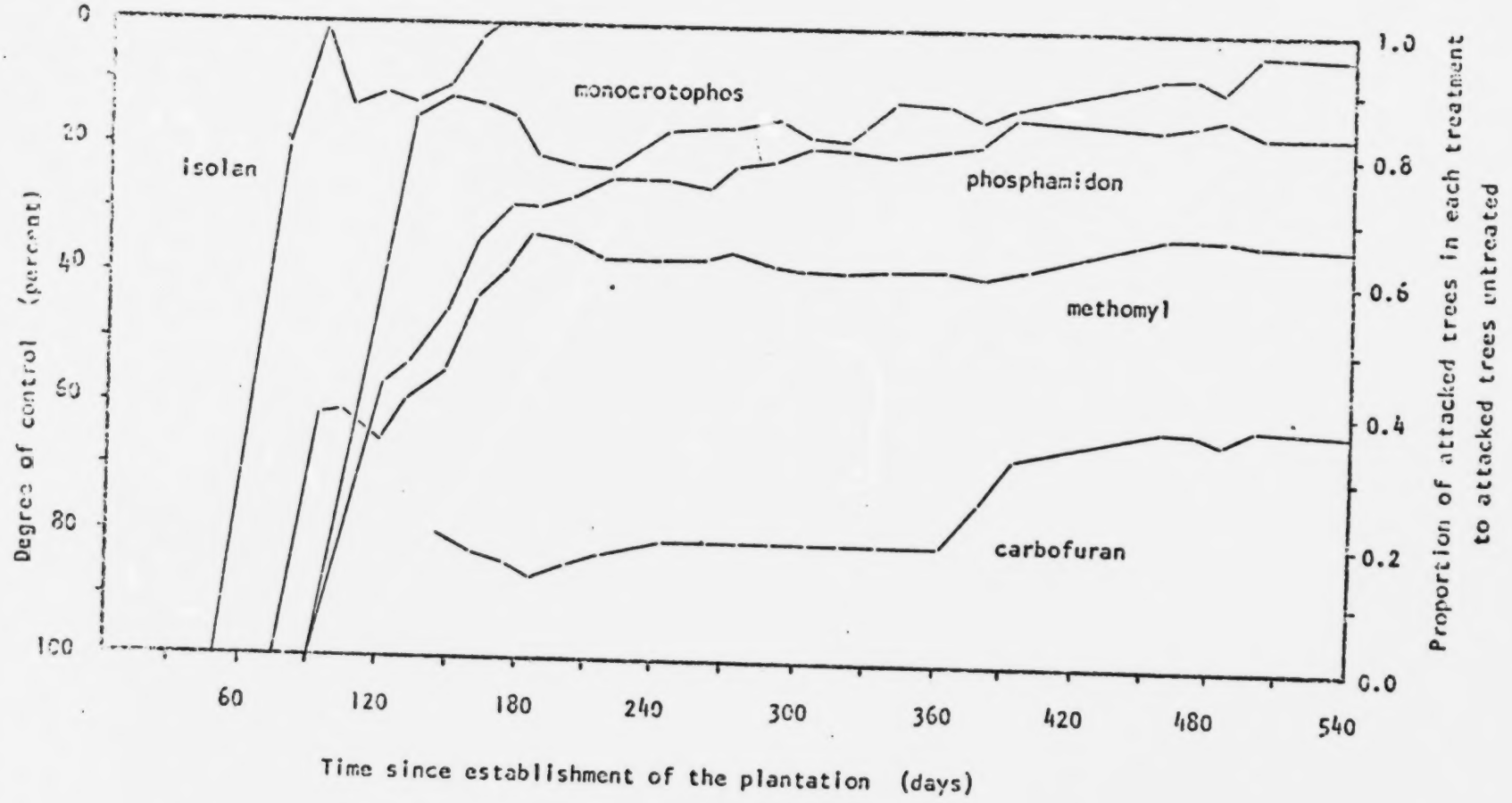

FIG. 10. THE DEGREE OF CONTROL, EXPRESSED AS THE RATIO OF THE PERCENTAGE OF ATTACKED TREES IN EACH TREATMENT TO THE PERCENTAGE IN THE UNTREATED GROUP AT PUENTE CAJON.

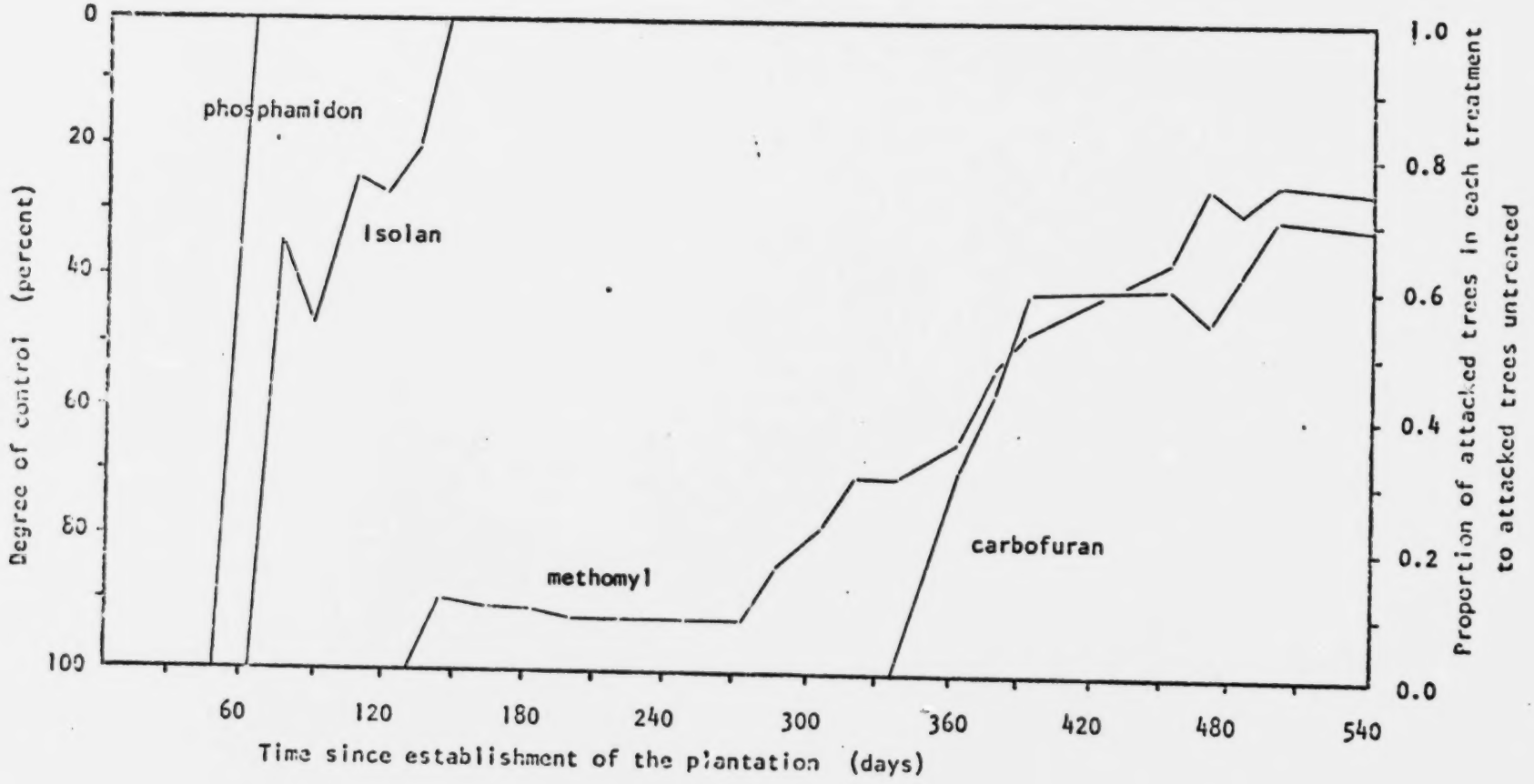

FIG. 11. THE DEGREE OF CONTROL, EXPRESSED AS THE RATIO OF THE PERCENTAGE OF ATTACKED TREES IN EACH TREATMENT TO THE PERCENTAGE IN THE UNTREATED GROUP AT FLORENCIA SUR.

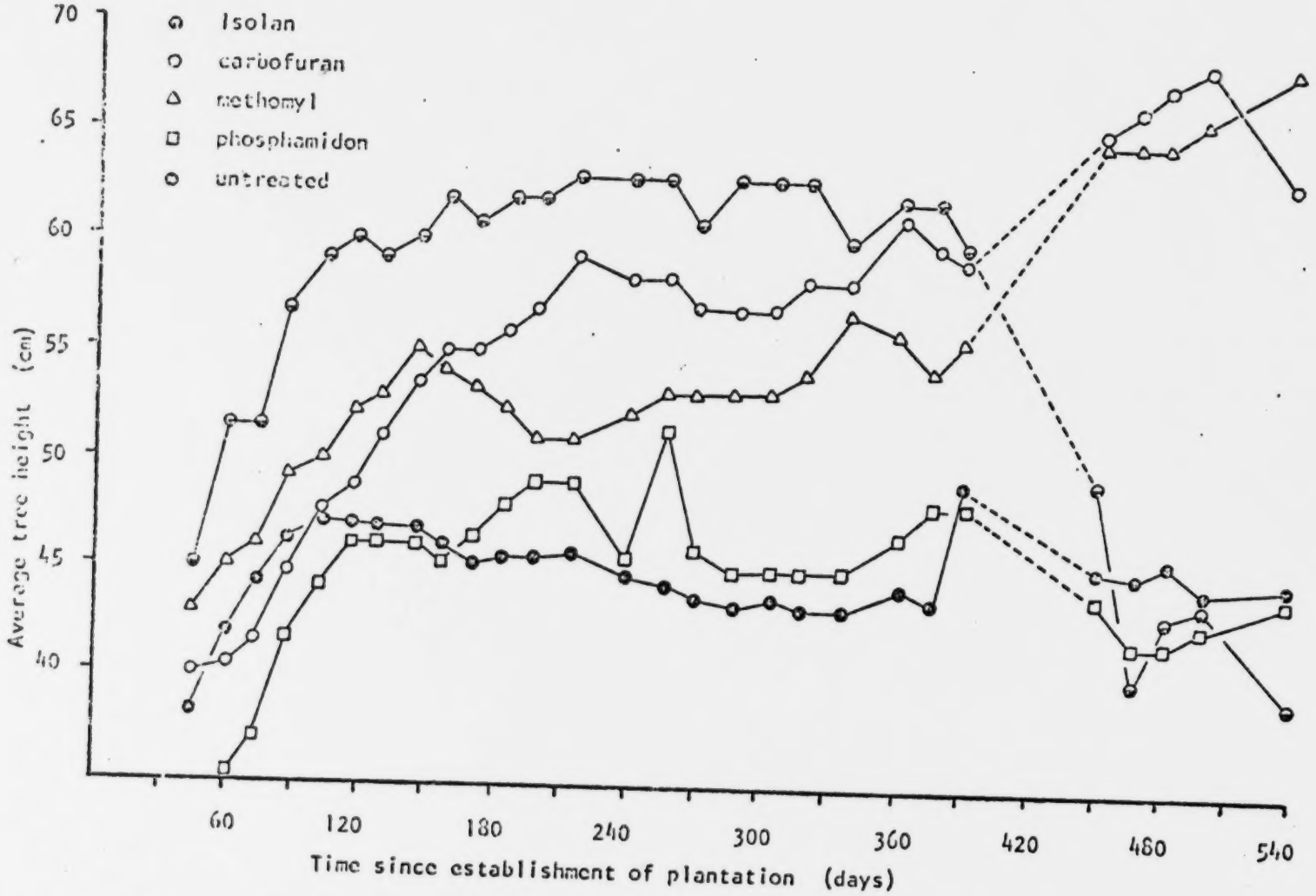

FIG. 12. THE AVERAGE HEIGHT OF TREES IN EACH TREATMENT GROUP AT PUENTE CAJON.

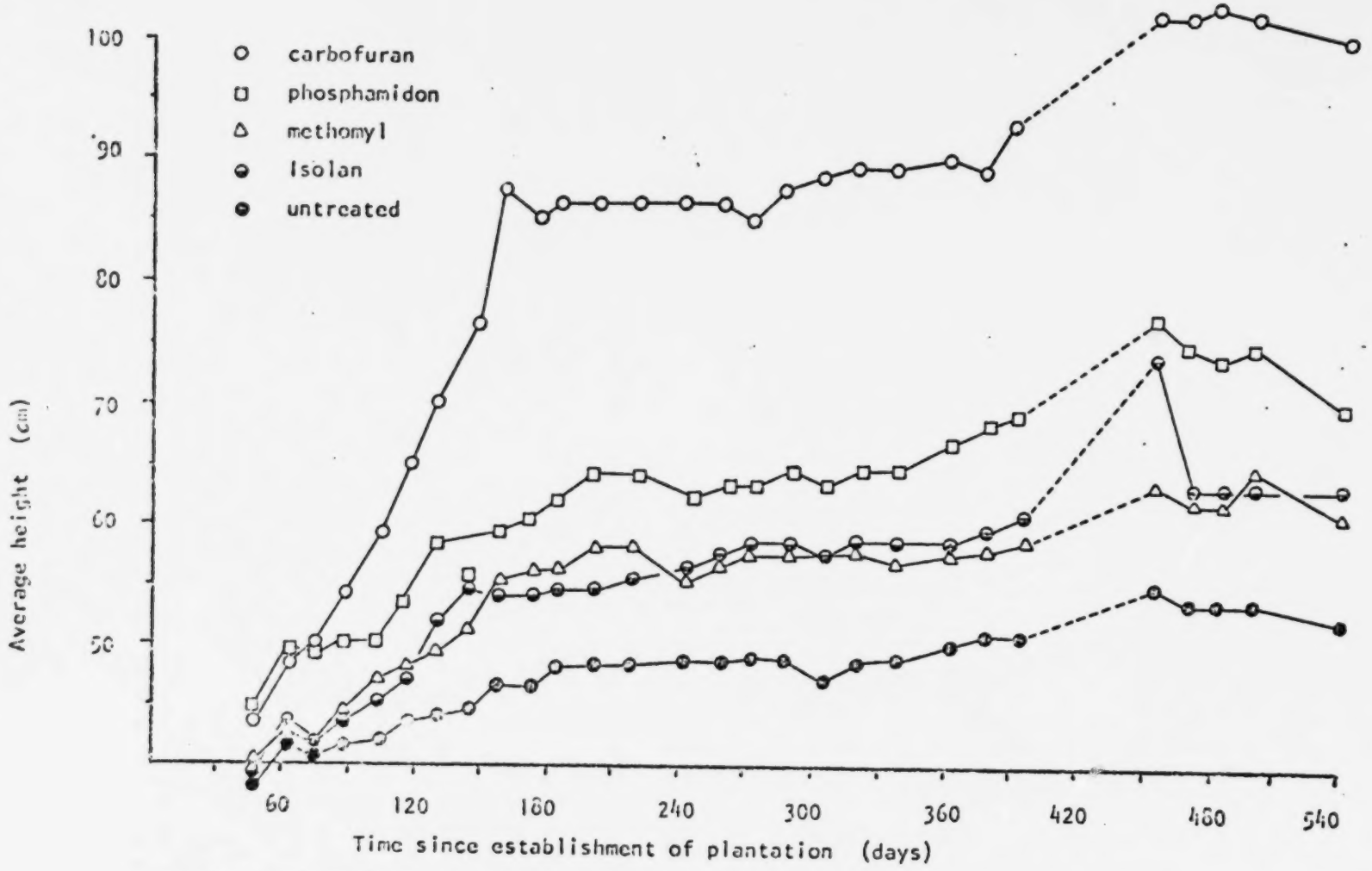

FIG. 13. THE AVERAGE HEIGHT OF TREES IN EACH TREATMENT GROUP AT FLORENCIA SUR.

TABLE XI

RESIDUE ANALYSIS BY REVERSE PHASE[a] THIN LAYER CHROMATOGRAPHY OF 5 SYSTEMIC INSECTICIDES

Insecticide	R_f	Sensitivity	days after soil treatment when leaf sample taken	insecticide concentration in leaf sample
methomyl	0.60[b]	5 ng	11	$\geqslant$10 p.p.m.
carbofuran	0.47[b]	8 ng	11	6 p.p.m.
Isolan	0.42,0.58[c]	$<$ 2 ng	6	50-100 p.p.m.
phosphamidon	0.73,0.82[c]	5 ng	6	$\leqslant$ 3 p.p.m.
monocrotophos	0.25[c]	2 ng	6	$\leqslant$ 1 p.p.m.

a immobile phase: water

b developed in petroleum ether

c developed in 20% benzene in petroleum ether

TABLE XII

THE RESIDUAL INSECTICIDE CONCENTRATION IN THE CONTROLLED RELEASE COMBINATIONS AT DIFFERENT TIMES AFTER PLACEMENT IN THE SOIL

combination	purity of the tech. insecticide	original concentration	conc. at 7 months[a]	conc. at 12 months[b]	conc. at 18 months[c]	Versamid 940 blank
carbofuran	97.1 %	24.9 %	19.0±2.3 %	17.2±2.3 %	16.5±2.7 %	0.001 %
methomyl	87.8 [d]	25.0	14.8±1	7.0±3	7.4±3	0.05 [d]
monocrotophos	96.7 [d]	25.0	--	10.2±1.5	7.3±1.5	0.02 [d]
phosphamidon	90.4 [d]	26.8	--	10.0±1.8	6.3±2.0	0.0002 [d]
Isolan	-- [e]	25.0	(6.3)	--	--	--

a average of 2 samples

b average of 4 samples

c average of 10 samples

d determined by elemental analysis (for S,P or Cl)

e not determined

TABLE X III

TREE HEIGHTS (cm) AVERAGED FOR EACH TREATMENT GROUP
IN THE PLOT AT PUENTE CAJON

	Controlled release treatment					
days after application when observation made	untreated	Isolan	phosphamidon	carbofuran	methomyl	monocrotophos
46	38.7	45	32	40	43	32
58	42.8	52	35	41	45	37
73	44.6	52	37	42	46	42
87	46.6	57	42	45	49	48
95	47.7	59	44	48	50	53
115	47.5	60	47	49	52	55
127	47.3	59	48	52	53	52
141	47.1	60	47	54	55	54
155	46.1	62	46	55	54	55
169	45.5	61	46	55	53	55
183	45.8	62	48	56	52	55
201	45.8	62	49	57	51	56
219	45.8	63	49	59	51	59
244	44.6	63	49	58	52	57
259	44.3	63	52	58	53	56
272	43.1	61	47	57	53	56
286	42.9	63	45	57	53	57
303	42.9	63	45	57	53	57
319	43.3	63	45	58	54	60
340	43.3	60	45	58	57	60
361	44.1	62	47	61	56	59
375	43.7	62	48	60	54	54
389	49.1	59	48	59	56	55
451	45.4	49	44	65	65	54
466	45.2	40	42	66	65	53
482	45.8	43	42	67	65	53
499	43.8	44	43	68	66	53
541	44.4	39	45	63	68	54

TABLE XIV

TREE HEIGHTS (cm) AVERAGED FOR EACH TREATMENT GROUP
IN THE PLOT AT FLORENCIA SUR

Controlled release treatment

days after application when observation made	untreated	Isolan	phosphamidon	carbofuran	methomyl	monocrotophos
46	37.5	39	44	43	40	32
58	41.6	43	49	48	42	36
73	40.5	41	49	50	41	35
87	41.6	43	50	54	44	35
95	41.9	45	50	59	47	34
115	43.6	47	53	65	48	26
127	44.2	52	58	70	49	26
141	44.8	55	55	77	51	23
155	46.7	54	59	87	55	25
169	46.8	54	60	85	56	26
183	47.8	55	62	86	56	27
201	48.3	55	64	86	58	27
219	48.3	56	64	86	58	27
244	48.7	57	62	86	56	29
259	48.6	58	63	86	57	27
272	49.2	59	63	85	58	27
286	49.2	59	64	87	58	28
303	47.8	58	63	88	58	28
319	48.8	59	64	89	58	29
340	49.0	59	64	89	57	30
361	50.3	59	67	90	58	31
375	51.0	60	68	89	58	31
389	51.1	61	69	93	58	31
451	54.8	74	77	102	63	33
466	53.5	63	75	102	62	34
482	53.9	63	74	103	62	38
499	53.9	63	75	102	64	39
541	52.4	63	70	100	61	39

TABLE XV

THE NUMBER OF ATTACKS IN EACH TREATMENT GROUP IN THE PLOT AT PUENTE CAJON

Controlled release treatment

	untreated	Isolan	phosphamidon	carbofuran	methomyl	monocrotophos
number of trees in group :	56	10	10	10	11	3
days after application when observation made	number of attacks					
46	3	0	0	1	0	0
58	4	1	0	1	0	0
73	18	1	0	2	0	0
87	20	3	0	0	5	0
95	48	6	4	1	3	2
115	44	10	6	1	4	6
127	23	5	4	0	5	2
141	63	14	12	0	10	3
155	47	20	17	0	15	1
169	47	18	13	0	14	2
183	23	6	7	0	2	0
201	5	2	1	2	2	0
219	7	7	3	1	0	0
244	2	0	0	1	0	1
259	1	3	0	1	0	0
272	0	1	0	0	0	0
286	2	1	1	0	0	0
303	3	5	2	0	0	0
319	2	1	0	0	0	0
340	4	1	0	0	1	8
361	15	0	11	0	0	0
375	13	10	8	9	0	0
389	3	5	5	3	0	0
451	3	1	0	2	4	1
466	0	0	0	0	0	0
482	4	0	1	0	0	0
499	5	5	0	2	0	1
541	0	0	0	0	0	0

TABLE XVI

THE NUMBER OF ATTACKS IN EACH TREATMENT GROUP IN THE PLOT AT FLORENCIA SUR

		Controlled release treatment				
	untreated	Isolan	phosphamidon	carbofuran	methomyl	monocrotophos
number of trees in group :	57	10	10	9	10	4
days after application when observation made	number of attacks					
46	0	0	0	0	0	0
58	2	0	1	0	0	0
73	11	1	0	0	0	1
87	15	1	5	0	0	0
95	22	2	2	0	0	0
115	10	3	5	0	0	0
127	6	1	5	0	0	0
141	12	5	7	0	1	0
155	6	4	5	0	0	0
169	7	1	2	0	0	0
183	2	1	0	0	0	0
201	3	1	0	0	0	0
219	3	2	2	0	0	0
244	0	0	0	0	0	0
259	0	0	0	0	0	0
272	2	1	1	0	0	0
286	2	2	2	0	1	0
303	4	1	1	0	1	0
319	2	0	0	0	1	0
340	0	4	3	0	0	0
361	2	0	1	11	1	0
375	8	0	2	6	2	0
389	30	2	6	12	8	1
451	23	9	8	2	6	0
466	13	2	3	0	5	0
482	6	0	2	2	0	0
499	11	1	3	3	5	0
541	2	2	2	0	0	0

The effectiveness of long-acting controlled release systemic insecticides was therefore demonstrated and the principle and merits of the controlled release concept further established.

EXPERIMENTAL

Phase 1

Materials. Kraft lignin (Indulin AT) was provided by Westvaco Corp., Charleston, S.C., while the Douglas-fir bark and sawdust was supplied by the Weyerhaeuser Co., Longview, Wash. The herbicides were provided by the Chipman Division of Rhodia, Inc., Portland, Ore., and by the Dow Chemical Co., Midland, Mich. Other starting materials and solvents were standard reagent grade.

Analysis. The composition of the combinations was calculated from the chlorine content determined by neutron activation analyses carried out with the nuclear reactor facilities at the University of Washington. Samples were irradiated for 2 min in a neutron flux of 1.8×10^{12} neutron/cm^2 sec, cooled, and counted by integrating the 1.60 MeV photopeak of ^{38}Cl with a 3 x 3 in. NaI (Tl) crystal and multi-channel analyzer.

Reaction Procedures.

Preparation of Herbicide Forest Solid Waste Combination. A mixture of the herbicide (1 mol), thionyl chloride (1.5 mol), and dimethylformamide (0.03 mol) was heated under reflux for 3 hr. Removal of the excess reagents by evaporation under reduced pressure afforded the acid chloride as a residue which was dissolved in benzene (200 ml) and added to a suspension of the dried powdered forest solid waste (400 g, moisture content <1%) in benzene (1000 ml) and pyridine (50 ml). After heating on a water

bath for 3 hr., the mixture was filtered, sequentially washed with benzene (1000 ml) and water (2000 ml), and air- and oven-dried at 105° to yield the herbicide-forest solid waste combination.

Preparation of the Combination of a Herbicide Acid with Kraft Lignin. A mixture of the herbicide acid (1 mol), thionyl chloride (1.5 mol), and dimethylformamide (0.03 mol) was heated under reflux for 3 hr. The acid chloride isolated as previously described was dissolved in dioxane (750 ml), added to a solution of dried kraft lignin (750 g, moisture content <1%) in dioxan (1500 ml) and pyridine (80 ml), and heated on a steam bath for 3 hr. The reaction mixture was then concentrated to about half its bulk and added to vigorously stirred hexane (3000 ml).

The precipitate, collected by filtration, was dried at 105°, exhaustively washed with water, and redried to yield the herbicide-kraft lignin combination.

Phases 2 and 3

Bioassay of the Controlled Release Solid Waste Herbicide Combinations. The soil used was an acidic (pH 6) Alderwood sandy loam comprising organic matter (15.2%), clay (15.1%), silt (22.7%), and sand (62.2%). About 150 g (dry weight) of soil was placed in a polypropylene cup with a drainage hole. After pressing and moistening the soil, controlled release chemical combinations were placed on the surface of the soil in amounts containing between 10 to 100 mg of the active herbicide present in the combined form.

A little soil was sprinkled over the combination, lettuce seeds were added and covered with a little more soil and the whole was then wetted down. Additional lettuce seeds were added weekly by pressing them into the

surface. The number of seeds germinating compared to that in controls containing soil alone was noted at intervals. Different amounts of 2,4-D were also compared. The results from this experiment are given in Fig. 1, which gives the weight of available herbicide in each combination, and the length of time during which it prevented germination and growth of lettuce.

Phytoxicity of Controlled Release Combinations of 2,4-DB to Western Red Alder and Douglas-Fir Seedlings. Seedlings (2-3 year old) of Douglas-fir (Pseudotsuga menziesii [Mirb.] Franco) and western red alder (Alnus rubra, Bong.), supplied by the Department of Natural Resources of the State of Washington, were individually transplanted outside in Seattle on December 6, 1969, into pots containing a weed-free soil having a surface area of 140 cm^2. The soil used was an acidic (pH 6) Alderwood sandy loam comprising organic matter (15.2%), clay (15.1%), silt (22.7%), and sand (62.2%). In March, 1970, after the seedlings were well established, quadruplicate sets were treated with chemical combinations of 2,4-dichlorophenoxybutyric acid with Douglas-fir bark, distributed evenly over the surface of each pot, which was then sprinkled with more soil (150g). The three herbicide-bark combinations, prepared as previously described,[92,112] contained 31, 37, and 50% of releasable herbicide and were applied at levels of 10, 55, and 100g/pot. The weeds which had grown in the untreated pots were identified (Veronica filiformis, Hypochaerus radicata L., Trifolium dubium, Dactylis glomerata, Poa annua, and Agropyron repens) collected by cutting at ground level in March, 1971, oven-dried at 105° and weighed.

The heights of all trees were measured at the time of transplanting and also in September, 1970, and the data is recorded in Table V. The phytotoxic effect of the treatments was observed periodically (15 days) and assessed on individual seedlings using a percentage scale for the extent of crown

damage with values ranging from 10% for undamaged crowns to 100% for decedent crowns. The assessment of each of the four replicates was averaged to give the results expressed as percent kill and collected in Table V.

Phase 4

Field Testing of Controlled Release Pesticides.

Muddy Creek Field Trial. The field trial site is located near the town of Sedro Woolley, 100 miles north of Seattle. The land is state owned and managed by the Department of Natural Resources. Logging operations were completed in the winter of 1969 and the site was burned in August, 1970. It was a very good burn, clean, with no damage to the humus layer. Original species on this site before logging were hardwoods, Douglas-fir, cedar, and hemlock and others in the ratio of volume (MBF) 4,770, 706, 90, and 31, respectively.

Two to three year old Douglas-fir seedlings from the nursery of the Department of Natural Resources, Washington, were transplanted in the months of December, 1970 - January, 1971.

Experimental Plan: In March, 1971, after the seedlings were well established, twenty rectangular plots were selected having about 32-40 seedlings of Douglas-fir in each plot and an area of 500 square yards. Each individual seedling was labeled. Eight feet of chicken wire of 4 feet in width was placed around 8 seedlings in each plot to measure the effect of deer browsing.

The main bulk of controlled release bark/2,4-DB combination was manufactured by the Eastman Kodak Co. under our directions and contained 37% of releasable herbicide. The combination was applied at levels of 200, 500,

1250, and 2000 g/seedling. Sixteen seedlings in each plot and an area of 25 square feet around each seedling, were treated with the combination. The rest of the seedlings were not treated and acted as buffers.

The heights of all seedlings were measured in the months of March and also in September, 1971, and the data is recorded in Table VIII. Visual measurements of weeds were taken after one growing season (Table IX). The weeds which had grown after one growing season were identified as Pteridium aquilinum (L.) Kuhn var. pubescens Undw., Poa annua L., Poa compressa L., Equisetum arvense L., Cirsium arvense (L.) Scop., Prunella vulgaris L., Sambucus callicarpa Greene, Rubus spp., Athyrium thelypteroides (Michx.) Desv., Polystichum munitum (Kaulf.) Presl.

Glenwood Field Test (Site 1). First year's results will not be available until October, 1972.

Glenwood Field Test (Site 2). First year's results will not be available until October, 1972.

Montesano Field Test. First year's results will not be available until October, 1972.

Thurston Field Test. First year's results will not be available until October, 1972.

Kirkland Field Test. First year's results will not be available until October, 1972.

Costa Rica Field Trial. Young potted Spanish cedar were treated with the systemic insecticides (75 mg active ingredient) in a manner similar to the translocation studies. Eggs of H. grandella were collected from Swietenia or Cedrela trees in IICA plantations around Turrialba. The eggs were contained on small bark slivers removed from the host trees. About 12 eggs then were taped to each of the test plants, generally to leaflets

midway on each leaf. This attempt to create an even distribution of emergent larvae was transient, due to the high mobility of the first instars. The attachment of the eggs to the plant was so timed, that when larvae emerged, the insecticide concentration in the foliage was at a maximum. This time of maximum insecticide concentration was determined by the bioassay with Drosophila for each insecticide under similar conditions, as described above. The time when the eggs were attached to the plant is indicated for some of the insecticides by the position of the arrows in Figs. 4-6; the average time for eclosion was two days after egg placement. Each tree was isolated by its placement and by a ring of a sticky substance spread around the base of the main stem.

In some cases, it was necessary to postpone the time of eclosion of collected eggs by placing them in a 8-9° cold box. This treatment, used for a maximum of six days, reduced the average rate of hatching from 80 percent for fresh eggs, to 70 percent, when desiccation was prevented.

Two days after attachment, the eggs were removed from the plants. The originally bright-red eggs changed to a white, transparent shell with a small hole if the larva emerged; otherwise the egg was black, brown, or simply collapsed. In this way, the number of larvae on the plant was determined. This deductive approach was necessary as the minute size of these first instars precluded extensive handling. A week after egg attachment, the plants were assessed for larval damage and compared with infested control plants containing no insecticides.

Damage was estimated for each tree by counting the number of dead leaves, the number of boreholes in the main stem, and by observing whether the leading shoot had been killed. The number of larvae still living was determined by brushing away all frass of the previous day and later watching

for production of fresh frass; the accuracy c s assessment was confirmed by dissecting some of the infested stems.

Phytotoxicity of Some Systemic Insecticides to Spanish Cedar. The phytotoxicity tests were carried out in the greenhouse under the same conditions as the previous bioassays and with similar potted C. odorata seedlings (height about 60 cm). The plants were watered daily. Temperature and soil were established as before. Single plants were treated with one insecticide dose; a series of plants received increasing quantities, approximately doubling, of each insecticide. Thus, a series of 6 plants received about 80, 160, 300, 600, 1000, and 5000 mg active ingredient respectively. The insecticides evaluated are given in Table X. The technical insecticides were applied to the soil surface as a water drench or if of low water solubility as an acetone solution, the solvent evaporated and the insecticide watered in.

The plants were then observed for visual signs of phytotoxicity. As time passed, the nature of the symptoms proceeded from mild to severe and in some cases, the plant died. From these observations, the sequence of symptoms was generally as follows: (A) spot burning on lower leaves, (B) tip burning on middle leaves, (C) yellowing of older leaves, (D) dropping of leaflets on lower leaves, (E) spreading of burn and yellowing of middle leaves (both spot and edge burning), (F) dropping of leaflets further up the plant, (G) dropping of denuded leaf axiles, (H) burning and yellowing of young leaves (chlorosis), (I) dropping of all leaves except leader, (J) distortion and dwarf growth of youngest leaves, and (K) loss of all growing leaves and leader in extreme cases.

Preparation of the Physical Controlled Release Polyamide Pellets. Polyamide resin, Versamid 940, lot number 0AB604 was used. Batches (300 g) were slowly melted (in metal containers) over a small flame with careful stirring so as to minimize incorporation of air bubbles. When molten, the calculated amount

(25% by weight) of the insecticide was mixed in and slowly stirred until completely dissolved and uniformly dispersed. The mixture was then quickly poured into molds made of short lengths (18 cm) of plastic garden hose (1 cm bore), sealed at the bottom end and attached vertically to a wooden frame. After cooling, the cylinders were removed by slitting open the molds and then cut into short lengths (2 cm or 8 cm) with a razor blade.

Five insecticides, carbofuran, methomyl, phosphamidon, monocrotophos and Isolan were converted into their controlled release combinations. The liquid technical insecticides (phosphamidon, monocrotophos and Isolan) dissolved readily and cast well. To dissolve carbofuran, the mixture was heated briefly to the melting point (150°). Some precautions were necessary with methomyl as it is unstable when heated over 110° (DuPont Bulletin). In this case, smaller batches (100 g) were used to reduce the duration of heating. As technical methomyl was not available, the 90% wettable powder formulation was used. The inert ingredient was sand.

Design of Field Trials of the Physical Controlled Release Insecticide Combinations. Two sites were chosen both located on IICA land. The locations were Puente Cajon and Florencia Sur in the Turrialba valley, both within a mile of the Institute. Both were sites of earlier plantings (September, 1967) of Cedrela odorata. In May, 1970, at Puente Cajon, 30 attacked trees remained and at Florencia Sur there were 27 attacked trees. In August, 1968, there were 38 and 42 surviving trees respectively[123] out of the original counts of 48. The reason for planting amongst the damaged surviving trees was to augment the number of Hypsipyla around the young plants and thus increase the intensity of attack.

Both sites are square, on even topography and each has an elevation difference diagonally, 1.5 m in the case of Florencia Sur and 1 m for

Puente Cajon. Both are easily accessible by all-weather roads. The site at Puente Cajon is surrounded by other species trial plots and second growth forest whilst that at Florencia Sur is bordered by coffee and Cadam plantations.

The soils of both sites are typical of the region having been derived from volcanic rocks. They are friable, dark brown soils with a granular texture and a good organic content. The pH varied between 4.5 and 5.3 for Florencia Sur and 5.4 and 6.2 for Puente Cajon. The site of Florencia Sur had been used for coffee while that at Puente Cajon had been used for sugar cane. As a result, the soil of Florencia Sur was the more fertile. In addition, Florencia Sur has good drainage in contrast to Puente Cajon which is poor.

The climate is described as that of Afi in the Köppen classification.[124] Based on information taken by the meteorological station at IICA, the average annual rainfall is over 2.6 m. Variability in rainfall is considerable; annual rainfall has been as low as 1.7 m and as high as 4.0 m. the average diurnal temperature range is 18-28°C. The annual range is small, the mean temperature varying from about 21° to 24°C. Typical of the area is the high relative humidity (average 90%) and high cloud cover (average daily sunshine, 4 hr).

Experimental Design. One level of treatment only for each insecticide was used. For Isolan, methomyl, monocrotophos and phosphamidon, this was 12 controlled release pellets 1 cm in diameter and 2 cm in length. For carbofuran, it was 12 pellets 1 cm in diameter and 8 cm in length. Other trees were treated with each insecticide in the technical grade form, or with controlled release pellets plus the "free" insecticide, or were untreated. This approach was to separate the effect of the controlled release insecticide.

For each insecticide, there was an equal number of trees of each treatment. Each plot of 100 trees was divided into 5 blocks of 20 and each block was again divided into 5 strips of 4 trees. Each strip was randomly assigned to each of the 5 insecticides and the 4 treatments (including control) were randomly distributed to individual trees within a strip. Thus, the design could be called a "random strip in block" configuration. Twenty trees were treated with controlled release combinations of each insecticide; only 7 trees could be treated with monocrotophos due to the short supply of this insecticide.

The experimental design is shown in Figure 14. Each square represents one tree, any treatment is indicated by a letter and a subscript: A = monocrotophos, C = carbofuran, M = methomyl, P = phosphamidon, and I = Isolan. For example: P_i means treatment with only "free" phosphamidon insecticide, P_p means treatment with controlled release pellets containing phosphamidon, and P_m is treatment with both free and controlled release phosphamidon. Controls (no treatment) are left blank.

The treatments with free insecticides were approximately at the same dosages administered in the greenhouse trials, i.e., about 100 mg active ingredient per plant, applied as a water solution or as granules which were watered in.

Establishment of Plantations. Seedlings (10 months old) of C. odorata were transplanted in the field with 2 x 2 m spacing in two plots at Puente Cajon and Florencia Sur having 100 trees each in a square (10 x 10) configuration. The following day (May 5, 1970), the controlled release pellets were inserted in the soil around the tree by first making a hole with an iron stake. The 12 pellets made an approximately 12" diameter circle with the pellets in a vertical attitutde. The depths of the pellets were: 3" for the

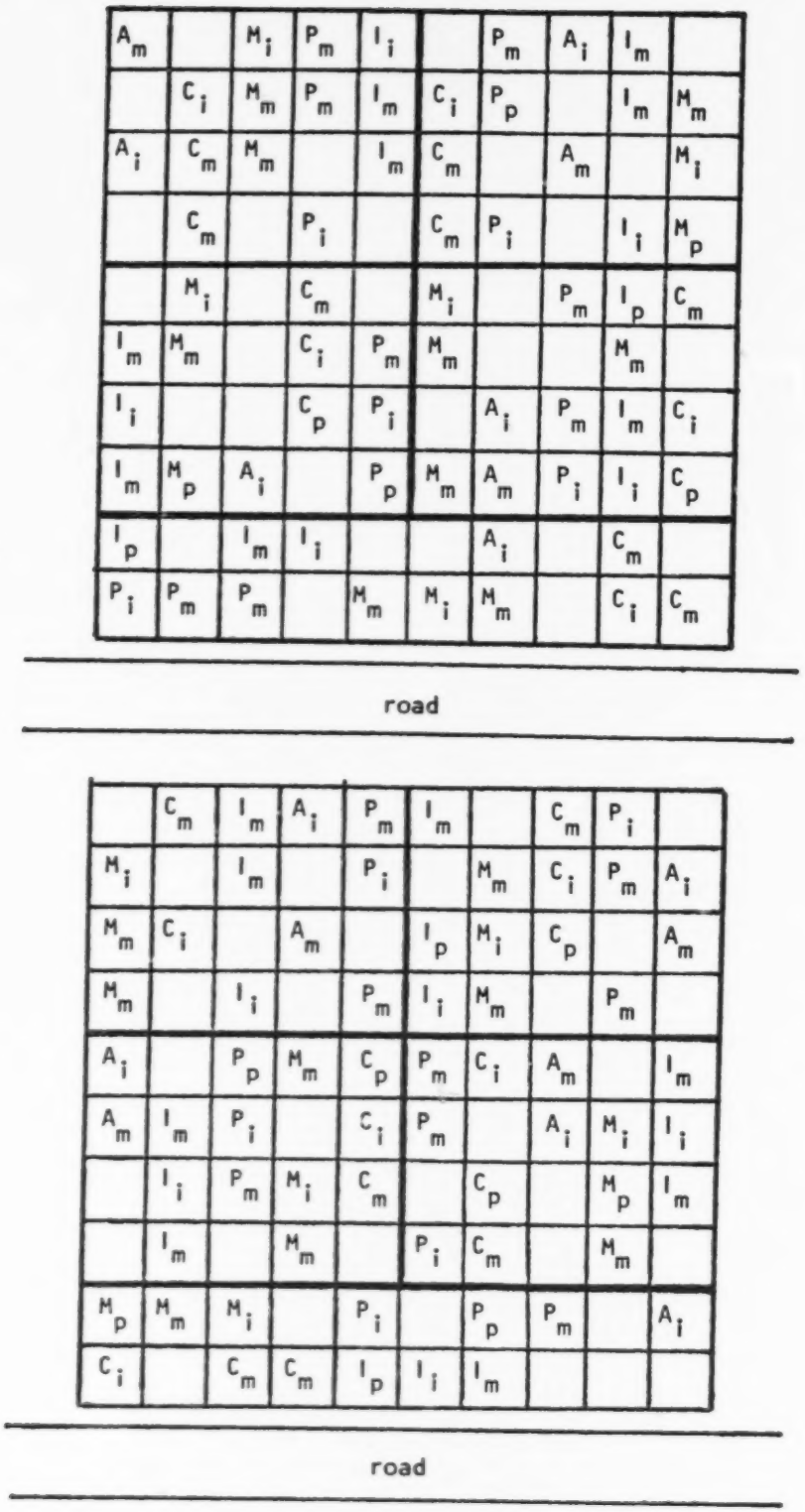

FIG. 14. EXPERIMENTAL DESIGN FOR THE FIELD TRIALS

2 cm long and 2" for the 8 cm long, as measured from the tops of the pellets. The free insecticides also were applied to the soil around the tree as described before.

To enable reliable observations to be made on the trees, a number of later precautions were taken. These included:

(a) replacing all weak and previously attacked seedlings,

(b) killing individual H. grandella larvae which had emerged from eggs laid on the plants before outplanting,

(c) all trees were watered and fertilized with 50 g of 20-20-0 granules, and

(d) to allow a period in which the controlled release insecticides could build up to a toxic level all plants were soil treated with 200 mg of either carbofuran or methomyl. The previous treatments of "free" insecticides (100 mg) were insufficient to provide reliable control.

Thus, by June 11, all the plants were healthy and established. This was a crucial time because a severe shootborer attack would disfigure the seedlings and prevent significant measurements being taken in the following months. In addition, it showed that methomyl and carbofuran were effective in protecting C. odorata in the field until 25-30 days after application. This period was necessary to allow the plants to spread their root systems to the region of the pellets in order to pick up sufficient insecticide.

Field Observations. In this study, the field experiments served a dual purpose. On one hand, the objective of the experiment was to determine if protection for an extended period was possible and on the other the host-pest system served as a bioassay for the rate of release of the insecticides. To obtain the maximum information from the experiment, a large number of observations were made at frequent intervals. Thus, every two weeks the following observations were made for every tree:

(a) the number of attacks, i.e., the number of active larvae as revealed by the occurrence of masses of fresh frass,

(b) the condition of the leader, whether healthy (A) or dead (D),

(c) the height of the plant, and

(d) visual signs of phytotoxicity, as evidenced by yellowing at tips or edges of the leaflets or by spots and loss of leaves. The degree of severity was categorized and represented by the designation: none --, slight I, moderate II, severe III.

CONCLUSIONS

1. Polymeric solid wastes, including much of urban garbage, containing a replaceable hydrogen atom can be used as a base for the preparation of controlled release pesticides.

2. A large amount of solid waste could be usefully recycled in controlled release pesticides.

3. Environmental pollution both by solid wastes and pesticides could be reduced by the use of controlled release systems.

RECOMMENDATIONS

1. Efforts to promote this method of recycling solid waste and reducing pesticide usage should be made by EPA.

2. Initially, attention should be concentrated on the control of vegetation in forests, under powerlines, on railroads, and in firebreaks.

3. Research, emphasizing field tests of solid waste pesticide combinations, should be continued.

SUMMARY

1. Practical methods have been developed to chemically combine pesticides with solid wastes containing replaceable hydrogen atoms.

2. Solid waste-pesticide combinations slowly release their active component to provide controlled protection.

3. The effectiveness of the controlled release solid waste-pesticide combinations is significantly greater than the corresponding quantity of uncombined pesticide.

4. Theories which permit the prediction of the period of effectiveness of solid waste-pesticide combinations have been developed and validated.

5. A chemical combination of 2,4-dichlorophenoxybutyric acid with forest solid wastes is selectively toxic to weeds and brush in the presence of Douglas-fir seedlings.

6. Controlled release forms of short-lived biodegradable insecticides have provided protection to Spanish cedar seedlings for more than 1 year under severe tropical testing conditions.

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